Synthesis Of Nucleosides

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1. Introduction

This chapter deals with the synthesis of nucleosides (e.g., the formation of *N*-glycosides of sugars such as D-ribose or 2-deoxy-D-ribose with heterocyclic nitrogen bases). The methods of nucleoside synthesis have been treated in a number of reviews and monographs. (1-7a)

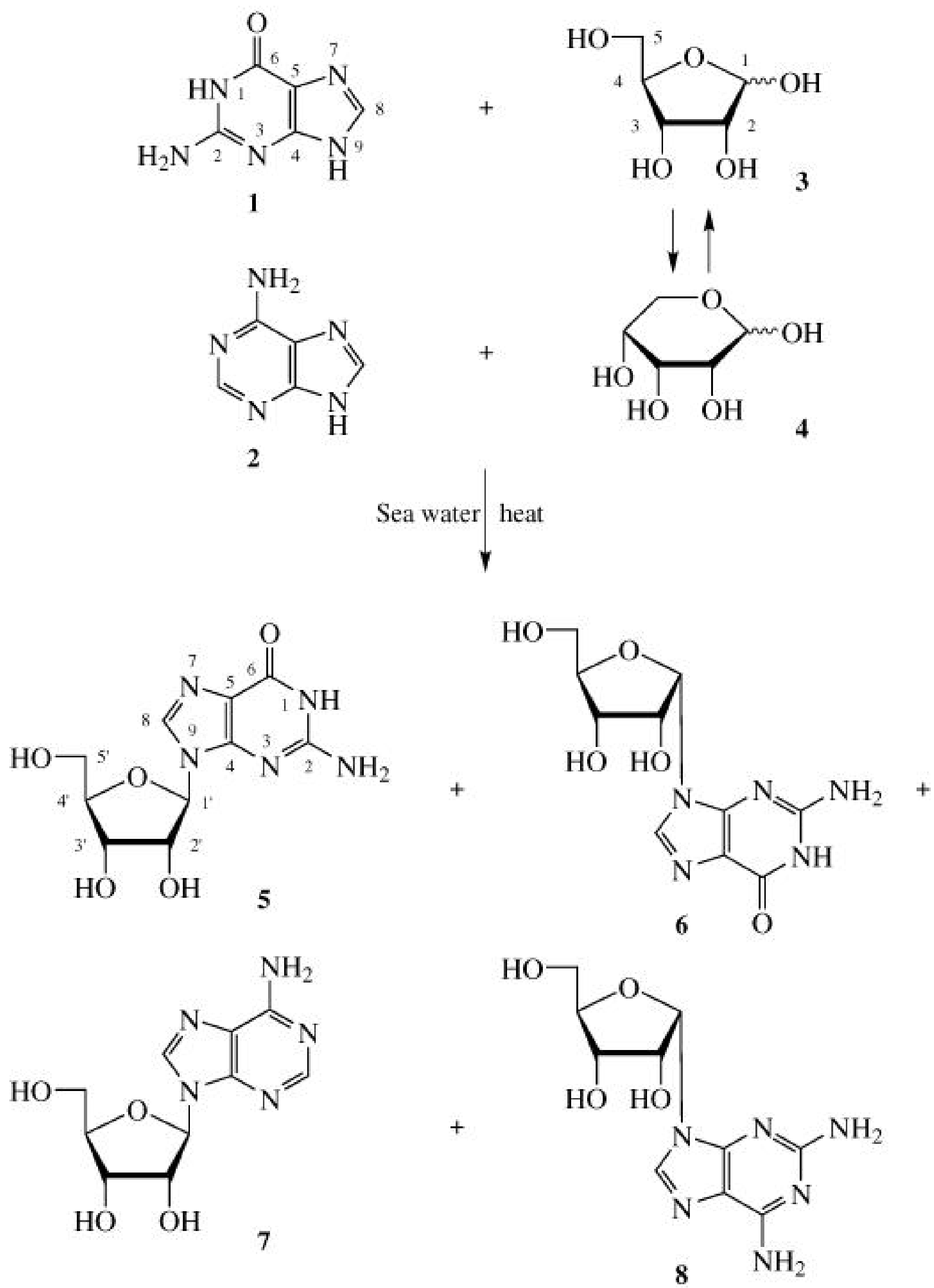
It is now generally accepted that nucleosides were among the first organic compounds formed at the start of evolution in the early history of our planet earth. To support this point, guanine (**1**) and adenine (**2**) were heated with D-ribose (**3** or **4**) in sea water, which contains the Lewis acid magnesium chloride as catalyst. (8, 9) One thus obtained the nucleosides guanosine (**5**, ca. 3%) and adenosine (**7**, 2.3%) together with comparable yields of the unnatural α -nucleosides **6** and **8**. The latter were gradually photoanomerized to the thermodynamically more stable **5** and **7** in overall yields of 5–6%. The furanose form of ribose (**3**) reacts faster than the pyranose form (**4**).

Corresponding syntheses of the pyrimidine nucleosides uridine (**11**) and cytidine (**12**) from uracil (**9**), cytosine (**10**) and ribose are more problematic and remain an enigma. The recent conversion of glycolaldehyde-*O*-phosphate and formaldehyde to ribose-2,4-di-*O*-phosphate (10) might give new insights into the prebiotic syntheses of **11** and **12**. The evidence and hypotheses for these prebiotic conversions and the evolution of RNA, as well as the implications of an “RNA World,” have been reviewed. (11-20c)

These RNA nucleosides are reduced in vivo as 5¢-*O*-diphosphates by ribonucleotide reductases (21-23) to the corresponding 2¢-deoxynucleosides—the building blocks of DNA such as 2¢-deoxy guanosine (see the atom numbering in **5**). The thermodynamically controlled synthesis of these four building blocks of RNA (**5, 7**, **11**, and **12**) has implications for the design of efficient, high yielding, new methods for the synthesis of the naturally occurring nucleosides, nucleoside antibiotics, (24) and modified nucleosides that may serve as antimetabolites to fight viral and parasitic diseases and cancer.

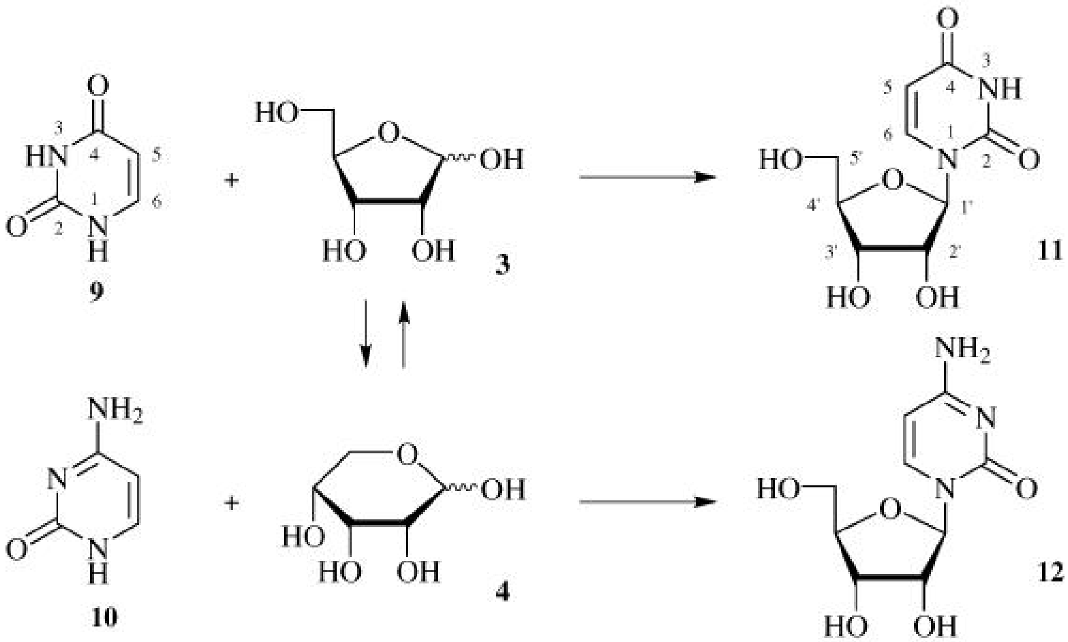
The nucleoside rings in this chapter are depicted arbitrarily in the *anti* conformation, as occurs predominantly in the crystal (25-32) and solution (based primarily on NOE-^{1}H- and ^{13}C-NMR measurements) (33-38) forms of pyrimidine nucleosides. Only a few nucleosides, such as 6-methyluridine, occur with the heterocyclic ring predominantly in the *syn* conformation. (25, 26)

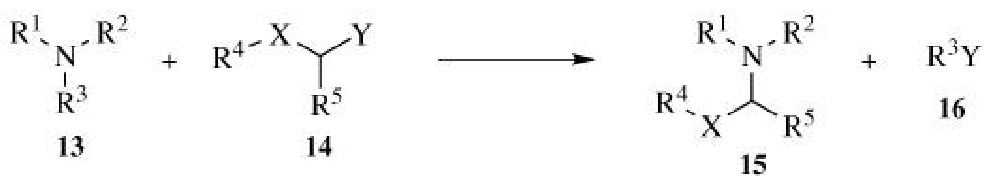
The synthesis of *C*-nucleosides has been reviewed previously (39-44) and is not covered in this review.



2. Scope and Limitations

We describe the synthesis of nucleosides from compounds **13**, in which R^1 and R^2 are carbon or nitrogen moieties that usually form a heterocyclic ring, and sugar derivatives **14**, in which R^4 and R^5 normally form a ring that bears the leaving group Y, to give the nucleoside **15** and R^3Y (**16**).

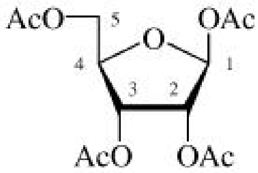




X = O, S, NCOR[45a-c]; Y = Cl, Br, F, OAc, OBz, $OC(NH)CCl_3$, SOMe, OH;
R^3 = H, TMS, Na, Li, HgCl, Ag

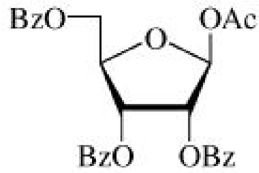
2.1. Sugar Moieties

Since we deal in this review with rather few protected sugar derivatives, these are introduced here.



17

1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose[46,47]



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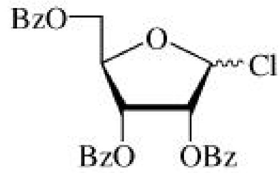
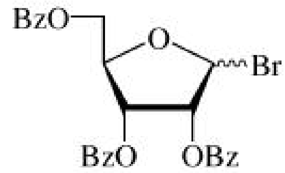
1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose[48]



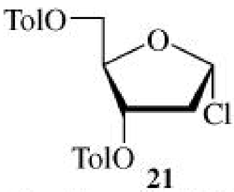
19

1-chloro-2,3,5-tri-*O*-benzoyl-D-ribofuranose[49]



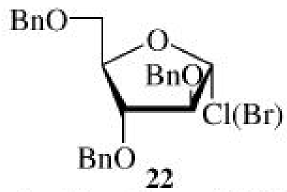
20

1-bromo-2,3,5-tri-*O*-benzoyl-D-ribofuranose[50]



21

1α-chloro-3,5-di-*O*-*p*-toluoyl-2-deoxyribofuranose[51]



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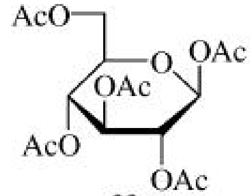
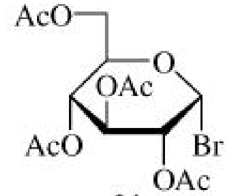
1α-chloro(bromo)-2,3,5-tri-*O*-benzyl-D-arabinofuranose[52,53]



23

1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose



24

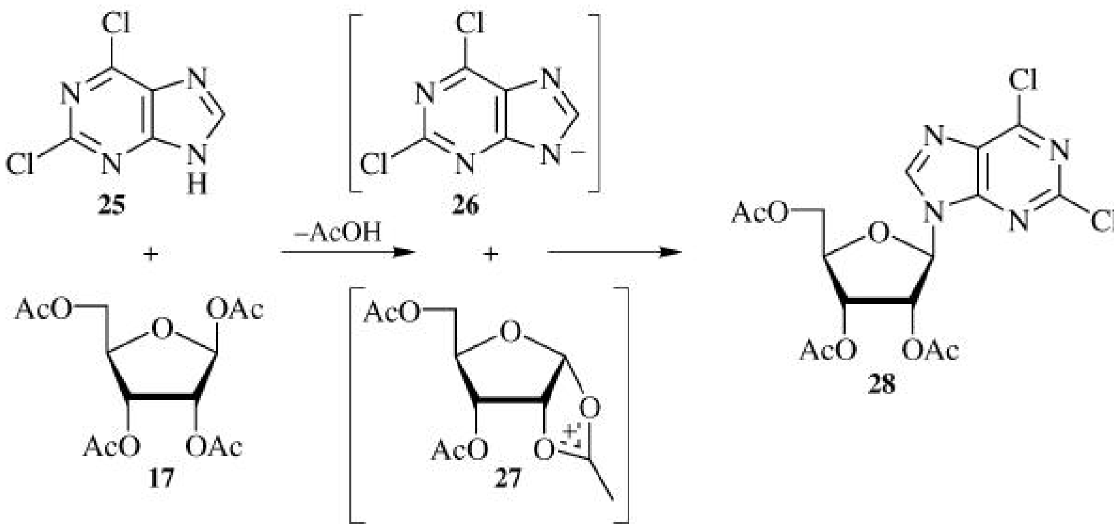
1α-bromo-2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose

3. Nucleoside Synthesis

There are three principal types of nucleoside-forming reactions: (a) The Fusion Reaction, (b) The Metal Salt Procedure, and (c) The Hilbert-Johnson Reaction.

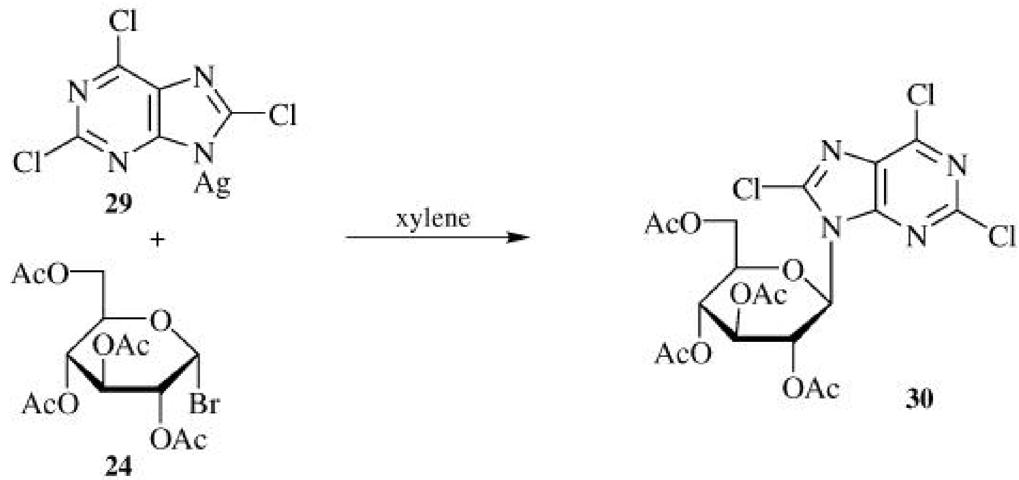
3.1. The Fusion Reaction

In this method acidic heterocyclic systems such as 2,6-dichloropurine (**25**) react with peracylated sugars such as **17** at 150–155° in a melt to form the assumed intermediates **26** and **27**, which combine in 54% yield to give **28** and the volatile acetic acid. (54, 55) This fusion reaction is usually performed in the presence of catalytic amounts of Lewis acids to promote the formation of the electrophilic sugar cation **27**; the reaction works with acidic systems such as substituted or annelated imidazoles, purineS, triazoles, or pyrazoles. Yields, however, seldom exceed 60–70% (see Ref. 55 for a review).



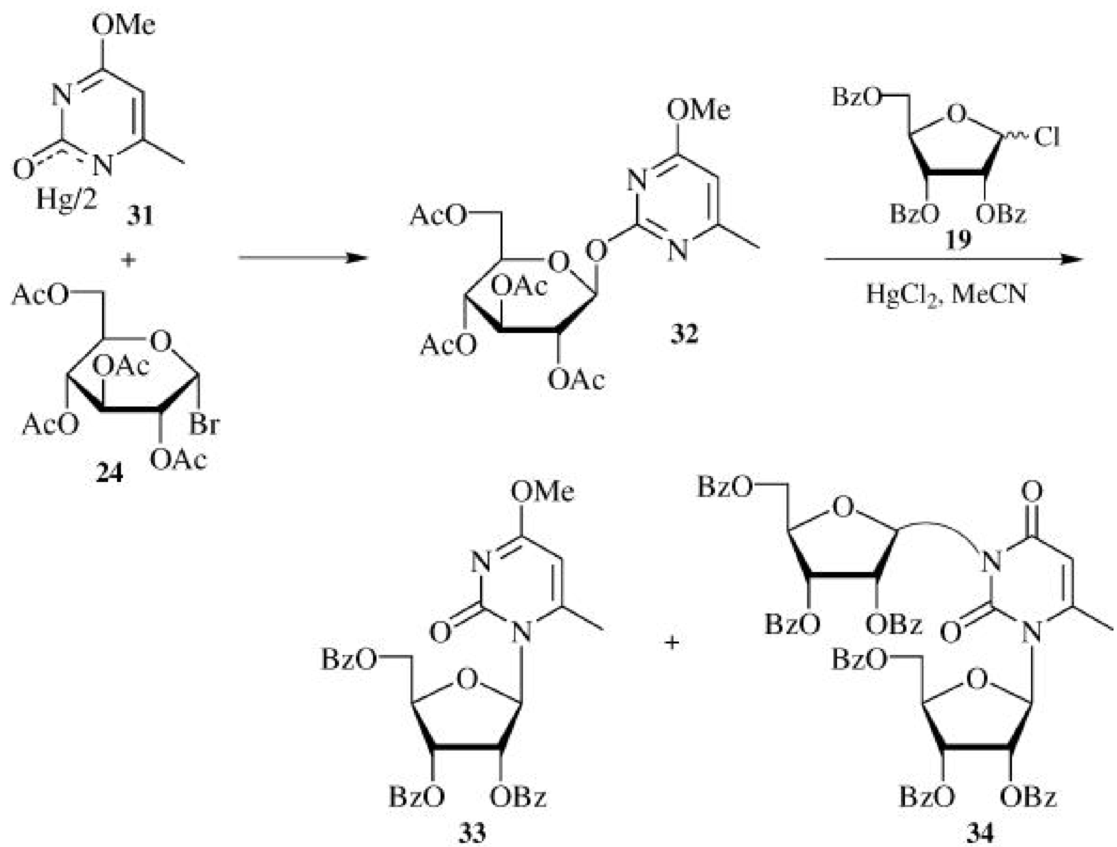
3.2. The Metal Salt Procedure

In this procedure metal salts of heterocyclic systems are reacted with protected sugar halides. In the original procedure, the silver salt of 2,6,8-trichloropurine (**29**) was heated with acetobromoglucose (**24**) (56) in xylene to give glucopyranoside **30**.

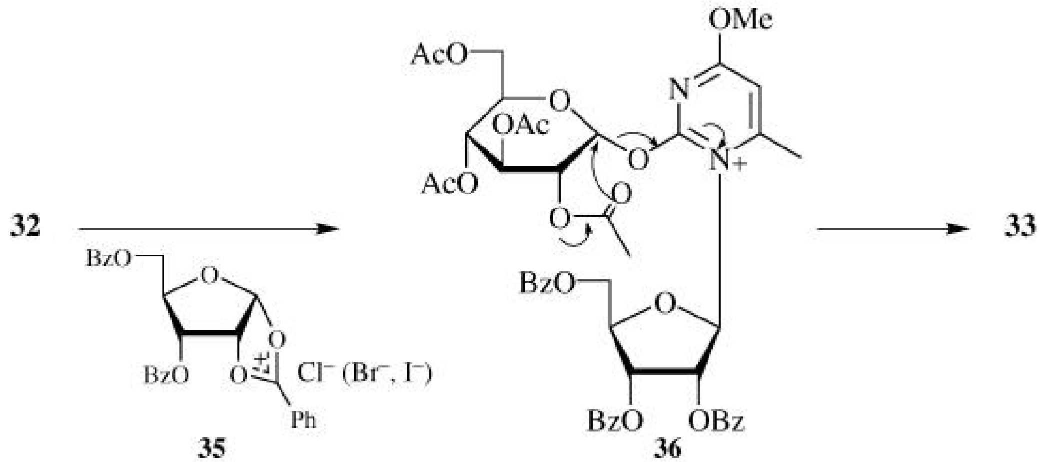


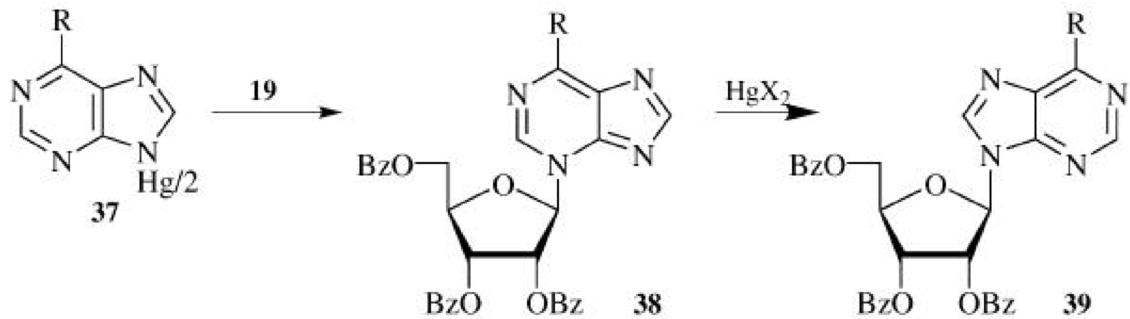
Because of the diminished polarity and thus better solubility (as well as reactivity) of mercuric salts compared with silver salts, investigators more recently have preferred the mercuric salts of heterocyclic bases, since the mercuric salt procedure often succeeds when the silver method fails. (1-5)

The initial products when using the mercuric salt procedure with uracils and cytosines are often *O*-glycosides such as **32**, which rearrange or react with another sugar halide to form the desired nucleoside. (57-59) Thus mercuric salt **31** reacts with **24** to give **32**, which is converted by excess **19** and added mercuric chloride in acetonitrile to nucleoside **33** and the N^1,N^3-bis(nucleoside) **34**. (60) Apparently, sugar cation **35** (derived from **19**) attacks the N^1 nitrogen in **32** to form intermediate **36**, which fragments to nucleoside **33**. The nucleophilic iminoether system in **33** can then react with additional cation **35** to give **34**.



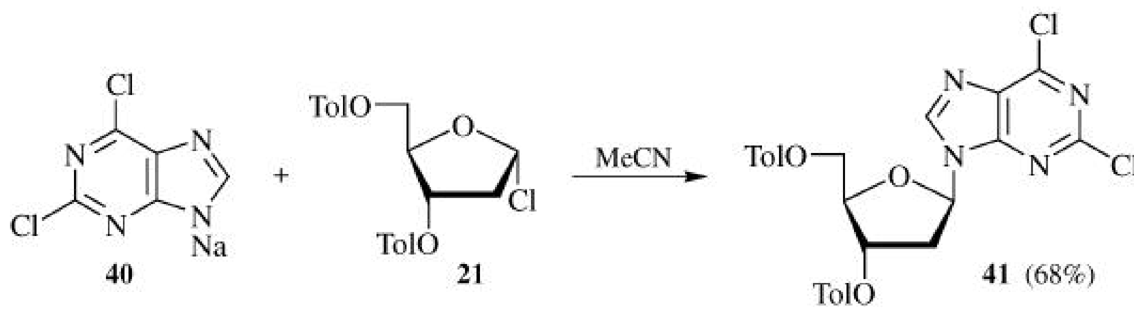
The mercuric salts of purines **37** can react with equivalent amounts of sugars such as **19** to give the kinetically controlled *N*[3]-nucleosides **38**, which rearrange on heating with $HgBr_2$, $HgCl_2$, or $Hg(CN)_2$ to the thermodynamically controlled "natural" *N*[9]-nucleosides **39** as well as some *N*[7]-nucleosides. (61) As in the rearrangement of the *O*-glycoside **32** to nucleoside **33**, the presence of reactive sugar cations such as **35** promotes the rearrangement of **38** to **39**. All of these mechanisms have been summarized and discussed. (61a)

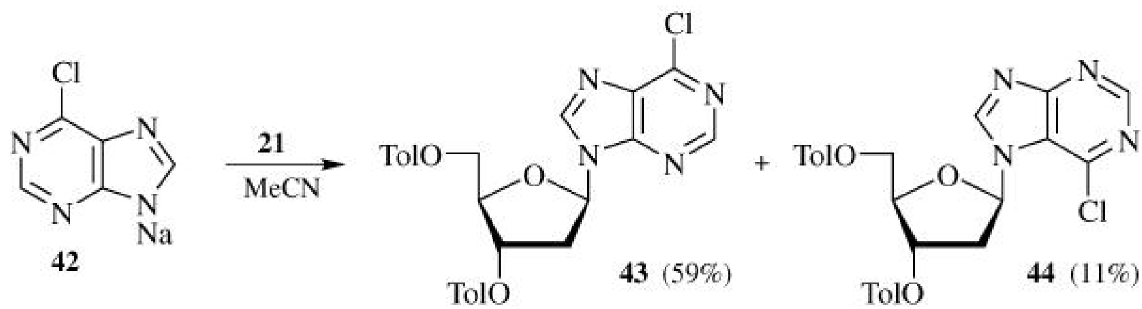




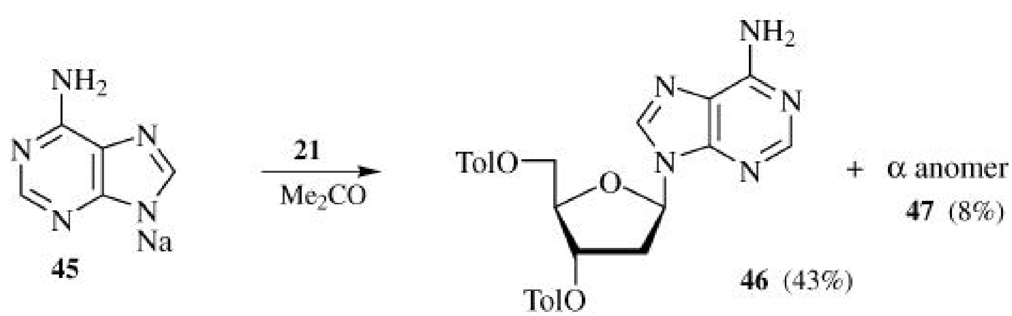
In addition to the often moderate yields and complicated mixtures obtained with the mercuric salt procedure, traces of mercuric impurities, which have strong biocidal properties, can falsify the biological data on the final nucleoside. (63), (63)

Recent important nucleoside syntheses employ the sodium salts of purines and related acidic heterocyclic systems, which are prepared in situ with NaH or analogous bases. These salts react with **21** in acetonitrile to give the corresponding β -nucleosides via an apparent S_N2 displacement of the 1 α -chlorine by the heterocyclic base. (64) Thus, sodium salt **40** reacts with **21** in acetonitrile to afford 68% of 2¢-deoxy- β -nucleoside **41**. The analogous reaction of the sodium salt of 6-chloropurine (**42**) with **21** gives 59% of the desired N^9-nucleoside **43** as well as 11% of the corresponding N^7-nucleoside **44**. Other authors report (65) that the isolated sodium salt of adenine (**45**) reacts best with **21** in acetone to afford directly

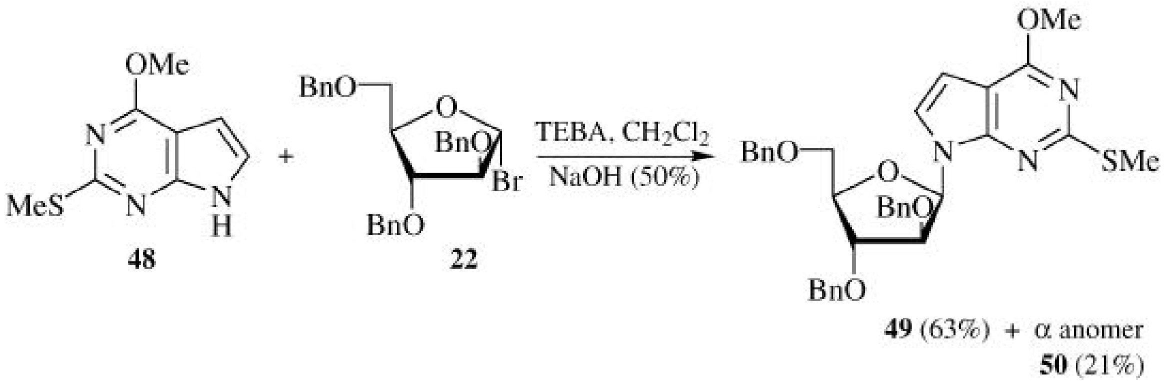




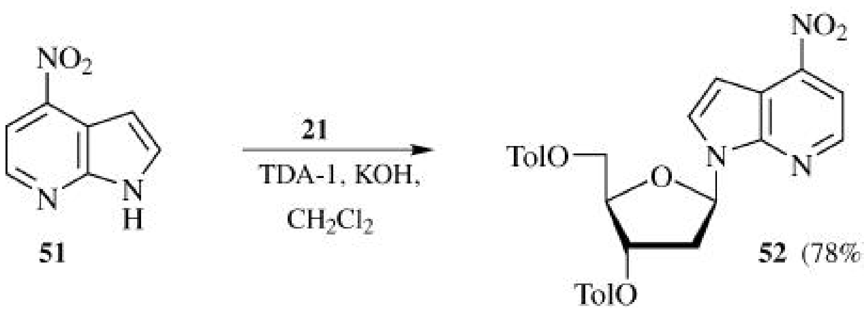
43% of the protected 2¢-deoxyadenosine **46** plus 8% of the α -nucleoside **47**, thus obviating the need for aminating the 6-chloro compound **43** to the unprotected 2¢-deoxyadenosine.

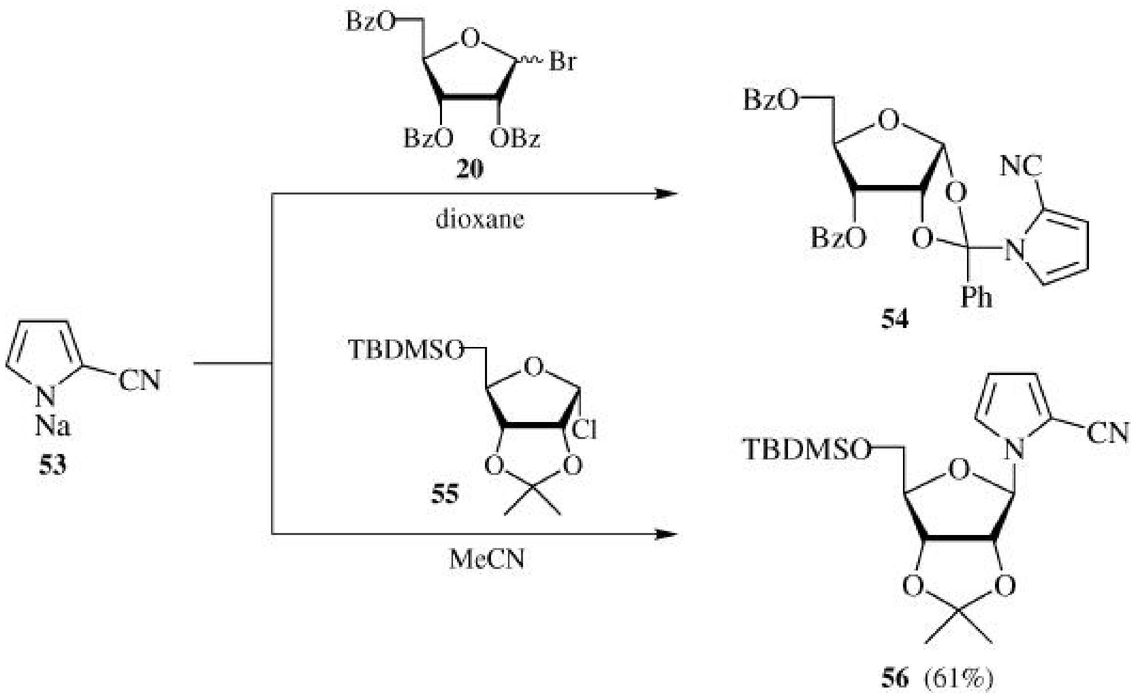


Equally effective are the phase-transfer glycosylations of heterocyclic bases such as 2-methylthio-4-methoxypyrrolo[2,3-*d*]pyrimidine (**48**), in which a standard N^7-glycosylation (e.g., by the Hilbert-Johnson method) is apparently not possible because the pyrimidine moiety is more nucleophilic than the pyrrole moiety. Thus, **48** is readily glycosylated by **22** in the presence of triethylbenzylammonium chloride (TEBA) and 50% aqueous sodium hydroxide to give 63% of β -nucleoside **49** as well as 21% of α -nucleoside **50**. (66) The acidic 4-nitro-1*H*-pyrrolo[2,3-*b*]pyridine **51** reacts analogously with **21** and tris[2-(2-methoxy)ethyl]amine (TDA-1) and KOH to afford **52** in 78% yield. (67) The sodium



salt of 2-cyanopyrrole (**53**) reacts with **20** to give orthoamide **54**, whereas the reaction of **53** with ribofuranosyl chloride **55** affords 61% of nucleoside **56**. (68)



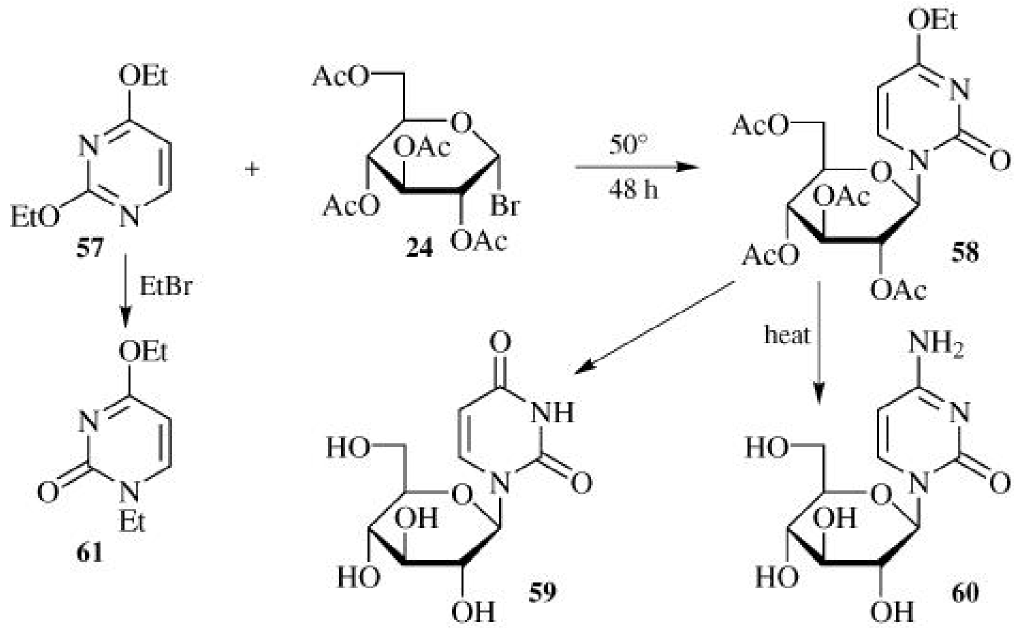


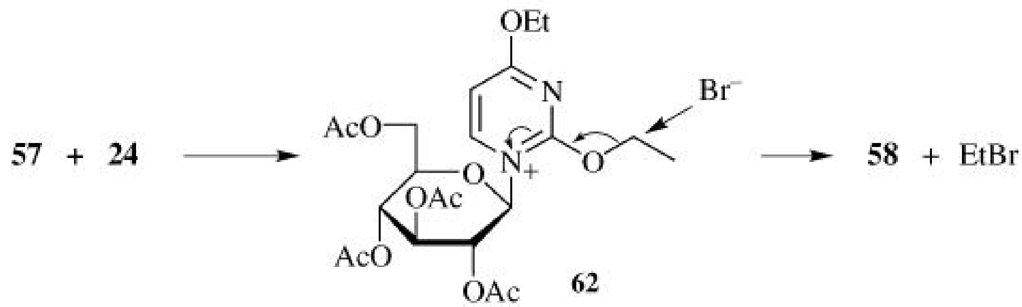
These methods employing sodium salts or phase-transfer reagents are quite efficient for the synthesis of 2′-deoxynucleosides (see the subsequent section on the synthesis of 2′-deoxynucleosides).

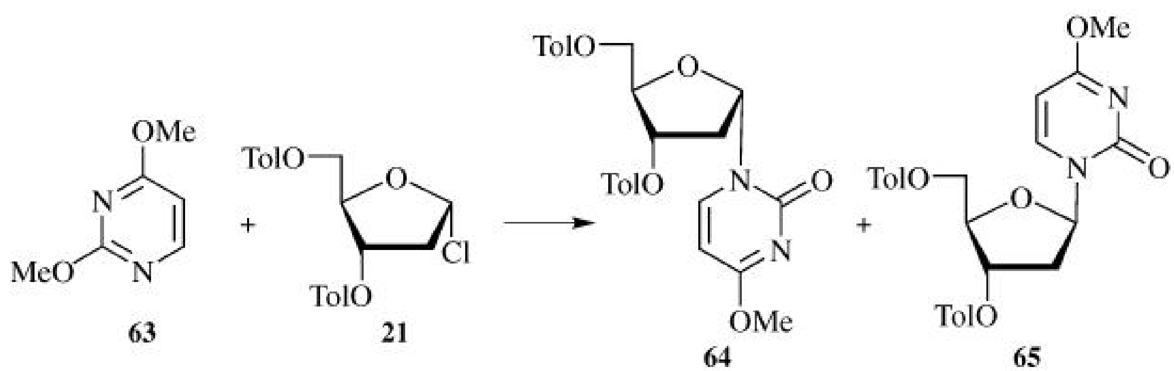
3.3. The Classical Hilbert-Johnson Procedure for the Preparation of Pyrimidine Nucleosides

In 1930 Hilbert and Johnson (69-71) reacted 2,4-diethoxypyrimidine (**57**) with **24** to give the protected intermediate **58** in ~ 30% yield. This intermediate can be saponified to the glycosylated uracil **59** or aminated by ammonia to the cytidine analog **60**. The liberated ethyl bromide can, however, convert **57** to the *N*-ethyl derivative **61**, thus diminishing the yields. It was later postulated that **57** and **24** react to give the N^1-alkylated intermediate **62**, which is then cleaved by bromide anion to afford **58** and ethyl bromide. (2, 70)

Reaction of 2,4-dimethoxypyrimidine (**63**) with **21** affords a mixture of α -anomer **64** and β -anomer **65** in which the α -anomer predominates. Several explanations for this unexpected behavior have been advanced, since an S_N2 reaction of the nucleophilic pyrimidine should lead predominantly to the β -nucleoside **65**. (72)







The classical Hilbert-Johnson reaction thus has a number of drawbacks:

(1) 2,4-dialkoxypyrimidines have to be prepared from the corresponding uracils via the corresponding 2,4-dichloropyrimidines; (2) yields are generally only

moderate owing to the formation of byproducts such as *O*-glycosides and *N*-alkylated products such as **61**; and (3) dealkylation of the resulting 4-alkoxy compounds with acids can cause difficulties, whereas the transformation of **58** into the cytidine analog **60** with ammonia under pressure at elevated temperatures proceeds without complications.

3.4. The Silyl-Hilbert-Johnson Reaction

Introduction of the Silyl-Hilbert-Johnson reaction by Birkofer, (73, 74) Nishimura, (75, 76) and Wittenburg (77) was a major advance. Silylation (e.g., with HMDS) converts the polar, often rather insoluble pyrimidine bases into lipophilic silyl compounds, which can be distilled and which are readily soluble in organic solvents, permitting homogeneous reactions. Because of the electron-releasing property of silicon, (78) the silylated heterocycles are better nucleophiles than the corresponding alkoxyheterocycles. The longer O-Si bond of 1.89 Å compared to the O-C bond of 1.53 Å makes the trimethylsilyl groups less bulky than a *tert*-butoxy group and results in the rapid solvolysis of remaining 4-*O*-trimethylsilyl groups. Because of the high mobility of the trimethylsilyl group one always obtains the thermodynamically most stable silylated heterocycle. (78a)

Silylated uracil **66** reacts with protected 1-halosugars such as **19** at room temperature in the presence of $HgCl_2$, $HgBr_2$, or $Hg(OAc)_2$ to afford the postulated intermediate **68**, which is cleaved by chloride or bromide ion to form 4-trimethyl-silyloxy compound **71** and the volatile Lewis acid trimethylsilyl chloride (**69**) or trimethylsilyl bromide as leaving groups. (77, 80) The 4-trimethylsilyloxy compound **71** can either be hydrolyzed in high yield to the 2,3,5-tri-*O*-benzoylated uridine **72** or reacted with primary or secondary amines to give the corresponding protected cytidines **73**. (79) Instead of adding mercuric salts, one can also heat **19** with **66** in absolute benzene or toluene or fuse **19** with **66** at temperatures up to 190° under reduced pressure in the absence of solvents. (76)

Finally, on reaction of **19** and **66** in benzene with silver perchlorate (or silver triflate) at room temperature, AgCl (or AgOTf) precipitates and the cyclic protected sugar perchlorate (or triflate) **67** is formed. Reaction of **67** with the silylated base **66** then affords intermediate **68**, which undergoes fragmentation by perchlorate (or triflate) anion to furnish **71** and the Lewis acid trimethylsilyl perchlorate (**70**) (or trimethylsilyl triflate). (74, 80)

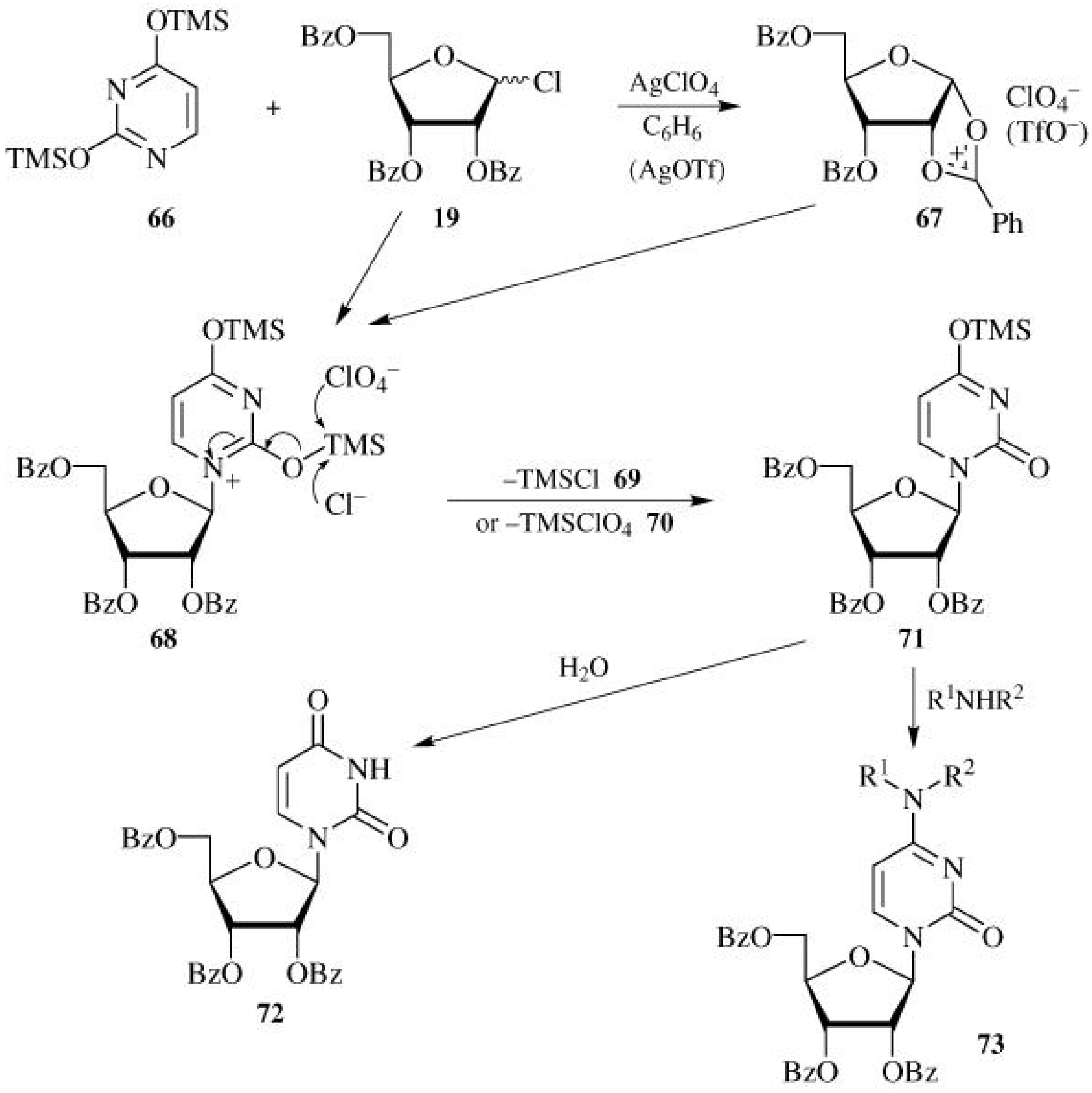
Because of the thermal instability of protected 1-halosugars such as **19, 20**, or **21**, reactions of silylated bases with mercuric salts or silver perchlorate in benzene at room temperature usually afford the best results. However, as mentioned before, use of mercuric salts gives rise to toxic impurities. (63) Thus the $AgClO_4$ procedure is preferable, affording high yields of protected nucleosides and protected 2-thiouridines and cytidines. (81)

It should be emphasized that all perchlorates are potential explosives; neat trimethylsilyl perchlorate explodes above 50°. (82) Importantly, nonexplosive triflate salts analogous to **67** can be obtained efficiently by treatment of 1-*O*-acyl- or 1-*O*-alkylsugar benzoates with trimethylsilyl triflate (TMSOTf).

4. Silyl-Hilbert-Johnson Reaction in the Presence Of Friedel-Crafts Catalysts*

4.1. Nucleoside Synthesis with $SnCl_4$ and Related Friedel-Crafts Catalysts

The Silyl-Hilbert-Johnson reaction of silylated 6-azauracil **74** with **19** in the presence of mercuric salts affords 6-azauridine-2′,3′,5′-tri-*O*-benzoate (**76**,

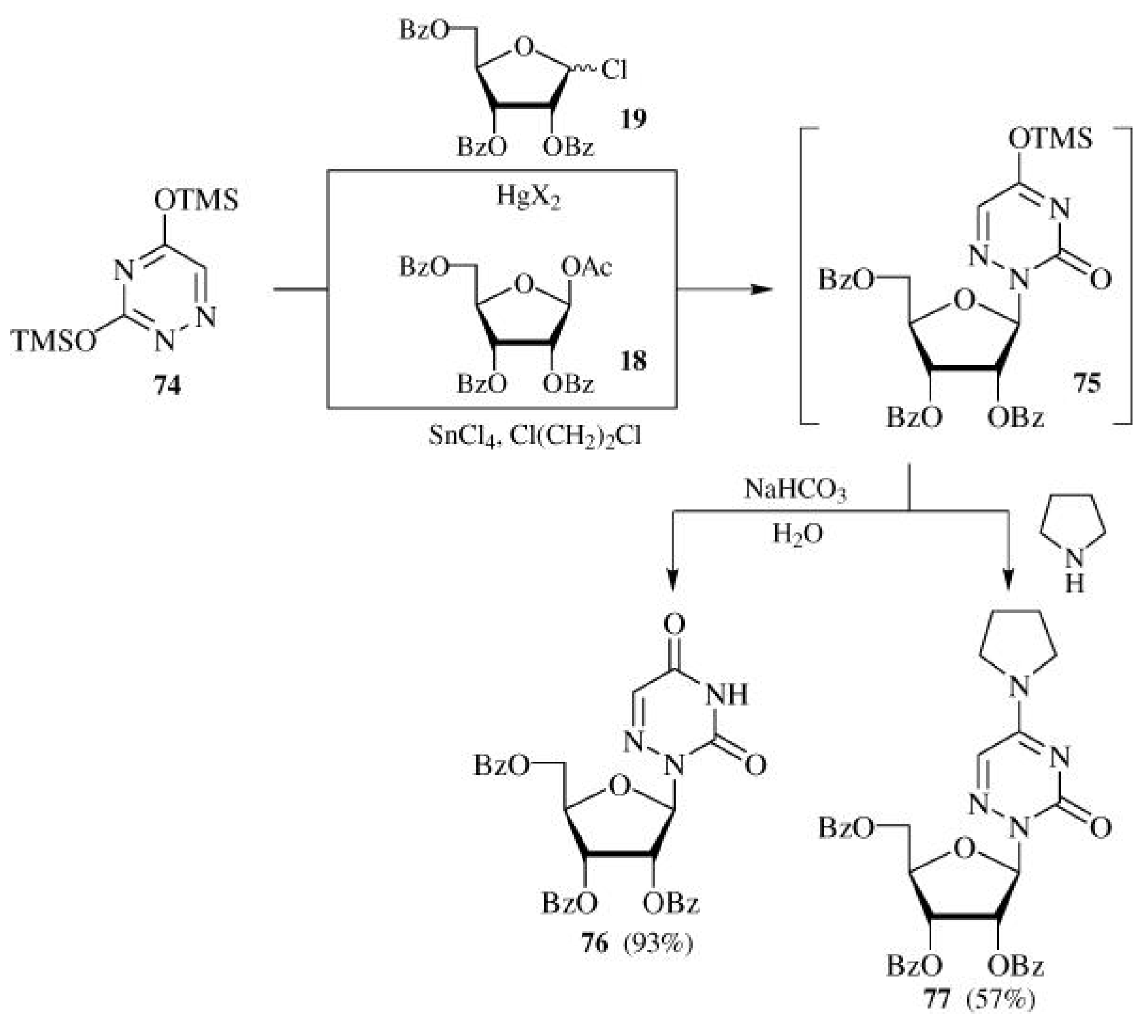


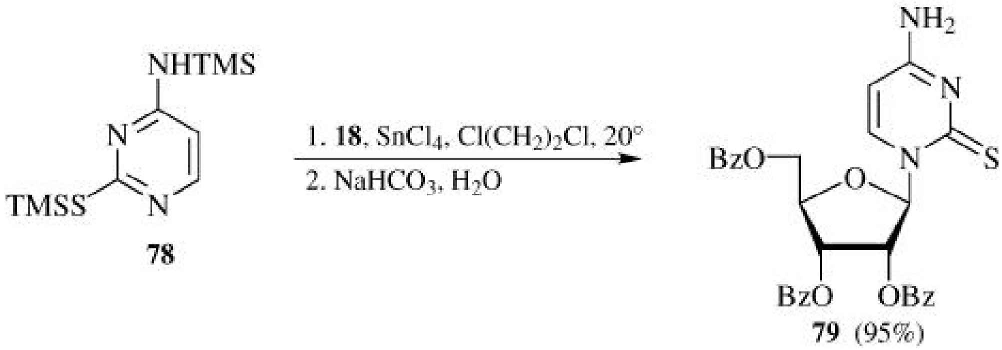
60%), as well as a series of colored impurities that apparently contain mercuric compounds. On the other hand, reaction of **74** with **18** in the presence of $SnCl_4$ or $TiCl_4$ in 1,2-dichloroethane at 20° affords crystalline **76** in 93% yield. (83, 84) The reactive intermediate **75** can be converted by excess pyrrolidine into the cytidine analog **77** in 57% yield. (79)

Friedel-Crafts catalysts such as $SnCl_4$ or $TiCl_4$ had been previously employed for the synthesis of purine nucleosides. (85, 86) For example, 1-*O*-acyl- or 1-*O*-alkyl-protected sugars were converted in situ into their corresponding reactive sugar cations such as **67** and then reacted with free purine bases, a technique which is still being applied. (86a-86b) However, Friedel-Crafts catalysts had not previously been used in combination with silylated heterocycles or any other silylated compounds such as silyl enol ethers. (87)

The reaction of silylated heterocyclic bases such as 2-thiocytosine (**78**) with **18** and $SnCl_4$ affords 2-thiocytidine-2′,3′,5′-tri-*O*-benzoate (**79**) in 95% yield. (84)

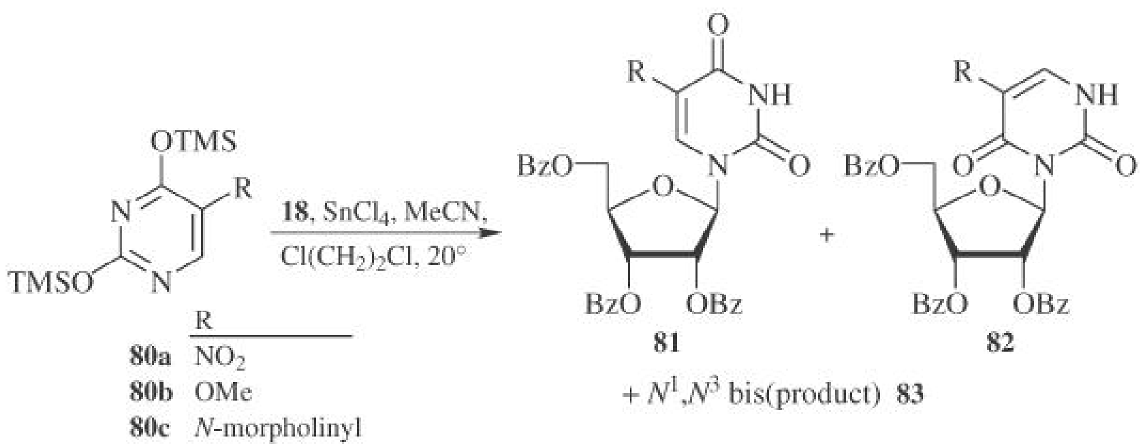
Surprisingly, the weakly basic silylated 5-nitrouracil **80a** reacts with **18** in the presence of ~ 10 mol % of $SnCl_4$ to afford
5-nitrouridine-2 ,3 ,5 -tri-*O*-benzoate





(**81a**) in nearly quantitative yield, (84) whereas the corresponding 5-nitro-2,4-dimethoxypyrimidine does not react at all with **21** under classical Hilbert-Johnson conditions. (88)

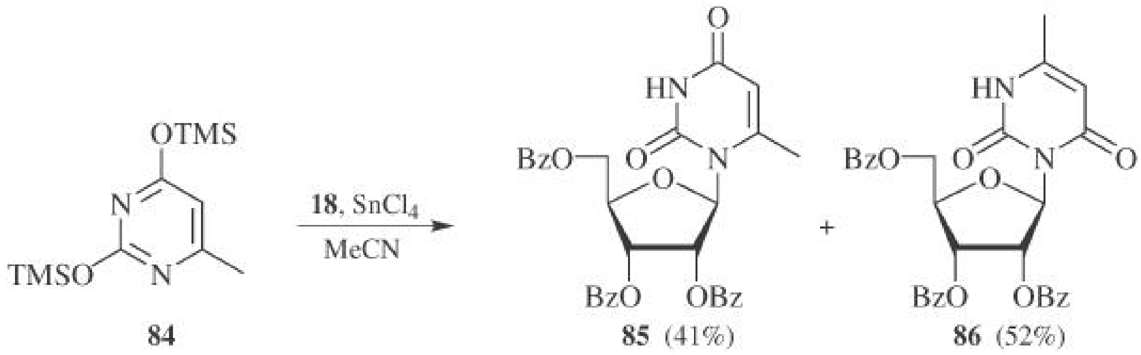
Compared to **80a**, the more basic silylated 5-methoxyuracil **80b** and silylated 5-morpholinouracil **80c** react with **18** much more slowly and only in the presence of excess $SnCl_4$ in acetonitrile to give 90% of **81b** together with **81c**, **82b**, and **82c**, in 53, 3, and 32% yields, respectively, along with the corresponding N^1,N^3-bis(nucleosides) **83**. The same reaction in the less polar 1,2-dichloroethane affords



even less of the desired N^1-nucleosides **81b** and **81c**. (90) In contrast to $SnCl_4$, the weaker Lewis acid TMSOTf gives much higher yields of **81b** and **81c** (see the following section).

In the aforementioned examples, it is primarily electronic factors that determine the N^1/N^3 ratio. With silylated 6-methyluracil **84**, however, steric as well as electronic factors determine the formation of protected 6-methyluridine **85** (89) as well as the protected N^3 product **86** and the N^1,N^3-bis(nucleoside)

87. (89a) Interestingly, nucleoside **85** in solution exists in the *syn* conformation (25, 26) owing to the interaction of the 6-methyl group with the sugar moiety.

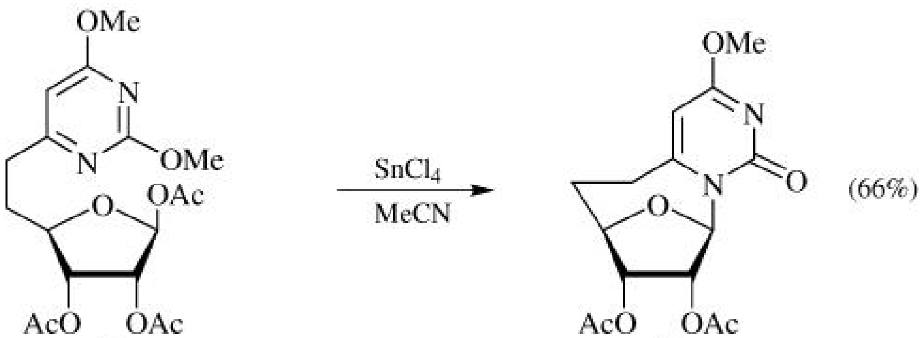


84 **85** (41%) **86** (52%)

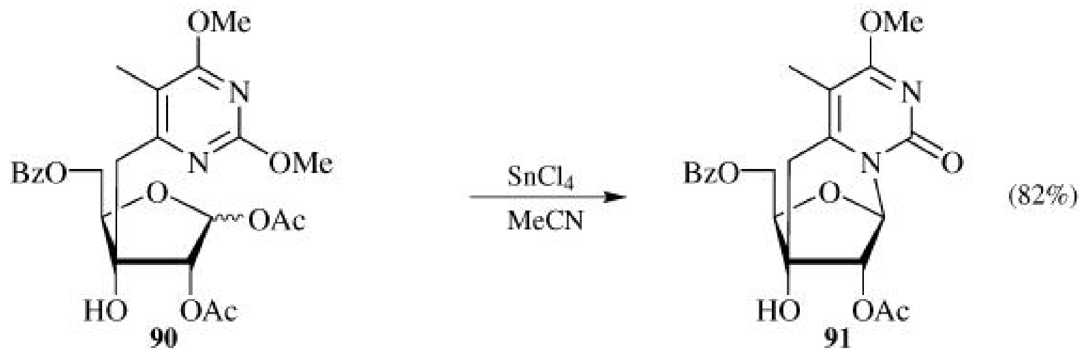
+ N^1,N^3 bis(riboside) **87** (3%)

Under optimal conditions employing carefully redistilled $SnCl_4$ and purified acetonitrile, 41% of **85**, 52% of **86**, and 3% of **87** are obtained, (89a) whereas much higher yields of **85** are again obtained with TMSOTf as catalyst (see the following section). No regiochemical problems are encountered in the intramolecular cyclizations of **88** and **90** with $SnCl_4$ in acetonitrile to form the nucleosides **89** and **91** in good yields. (91-93) For analogous cyclizations of silylated bases with Lewis acids see refs 94–97a-f.

In the $SnCl_4$-catalyzed Hilbert-Johnson reaction, other sugar moieties such as **21** can be employed to give high yields of 1:1-mixtures of the β - and α -nucleosides. Analogous reactions with the arabinose derivative **22**, peracylated

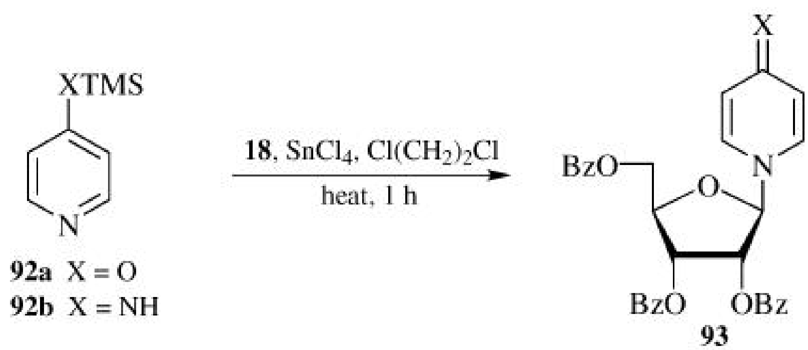


88 **89**



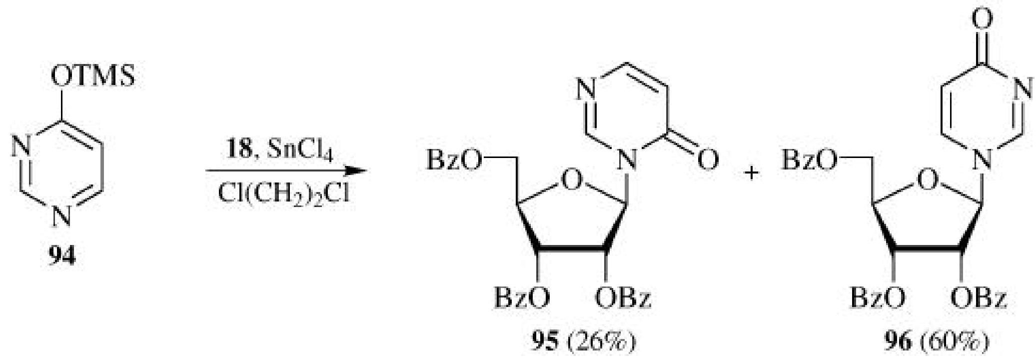
β -D-ribopyranose **23** (84) and acylated di- and polysaccharides (98) are summarized in Tables III and IV.

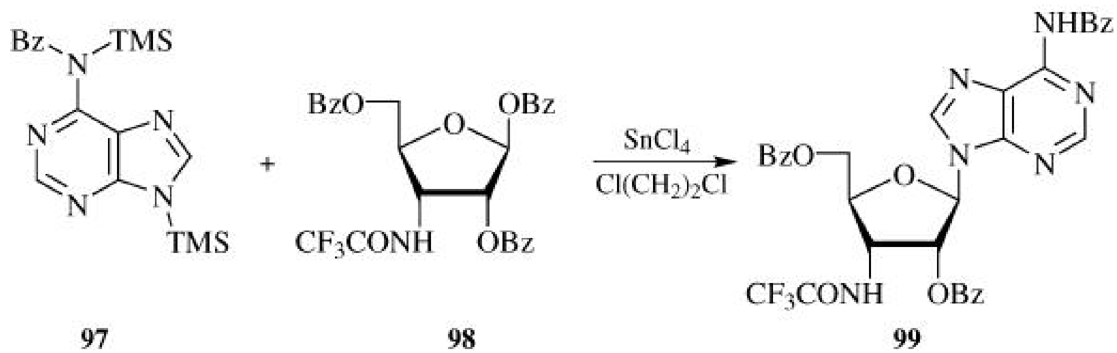
Although reaction of 4-trimethylsilyloxypyridine (**92a**) with **18** in boiling 1,2-dichloroethane in the presence of $SnCl_4$ gives nucleoside **93a** in 63% yield, the corresponding silylated 4-aminopyridine **92b** does not react under these conditions. Analogously, silylated pyrimidin-4-one **94** furnishes a mixture of 26% **95** and 60% **96**. (99)



The reaction of silylated purine bases such as disilylated N^6-benzoyladenine **97** with peracylated sugars such as **98** affords the corresponding purine nucleoside **99** in up to 70% yield. (100, 101)

In the reaction of silylated 6-azauracil **74** with **18**, other Friedel-Crafts catalysts such as $FeCl_3$,$BF_3{\cdot}OEt_2$, $AlCl_3$, or $TiCl_4$ also give good yields of 6-azauridine-2 ,3 ,5 -tri-*O*-benzoate (**76**). (84) Some research groups have subsequently



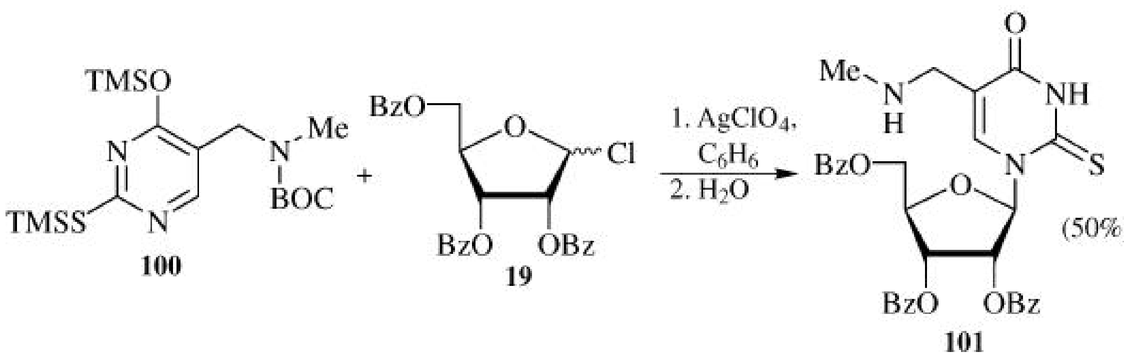


employed $BF_3{\cdot}OEt_2$, (102-104) $SnCl_2$, (105,106,106a,b,c) $SbCl_5$, (107-109) $ZnCl_2$, (110-112) ZnI_2, (113) $EtAlCl_2$ (114-117) or SiF_4. The latter boils at –86° and has been used in combination with protected 1-fluorosugars. (118) However, the majority of nucleoside chemists prefer either $SnCl_4$, which can be readily redistilled before use and gives homogeneous reaction mixtures in either 1,2-dichloroethane or acetonitrile, or the newer trimethylsilyl triflate (TMSOTf) or trimethylsilyl nonaflate. Newly developed Lewis acids for selective aldol reactions, such as $SnCl_4/Sn(OTf)_2/\ LiClO_4$, (119) $Sn(OTf)_2/Bu_2Sn(OAc)_2$, (120) $Cp_2ZrCl_2/\ AgClO_4$, (121) or Ph_3CClO_4 (122, 123) might also be applicable to nucleoside synthesis, as could the recently described combination of AgOTf and Ph_2SnS. (124) A direct comparison, however, shows that yields of nucleosides with other catalysts are essentially the same as those with trimethylsilyl triflate. (106c)

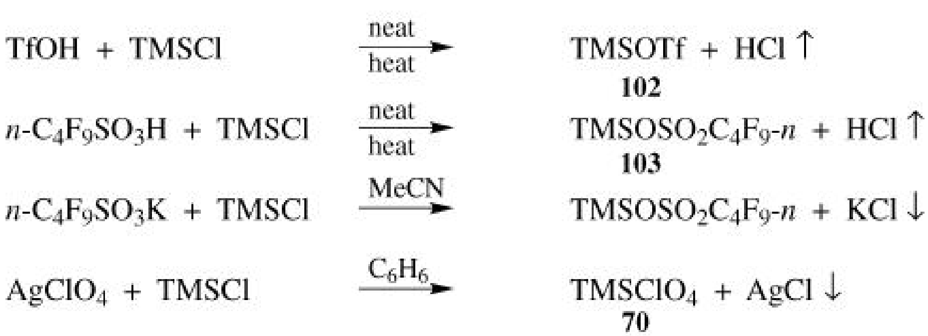
The Lewis acid should generally be just strong enough to convert protected 1-*O*-acyl-, 1-*O*-alkyl-, or 1-halosugars into their corresponding oxonium salts (such as **67**). Any additional acidic strength of the Lewis acid will only result in increased σ-complex formation with the silylated base, which in turn might lead to complications in regioselectivity or reaction rates.

4.2. Nucleoside Formation with TMSOTf

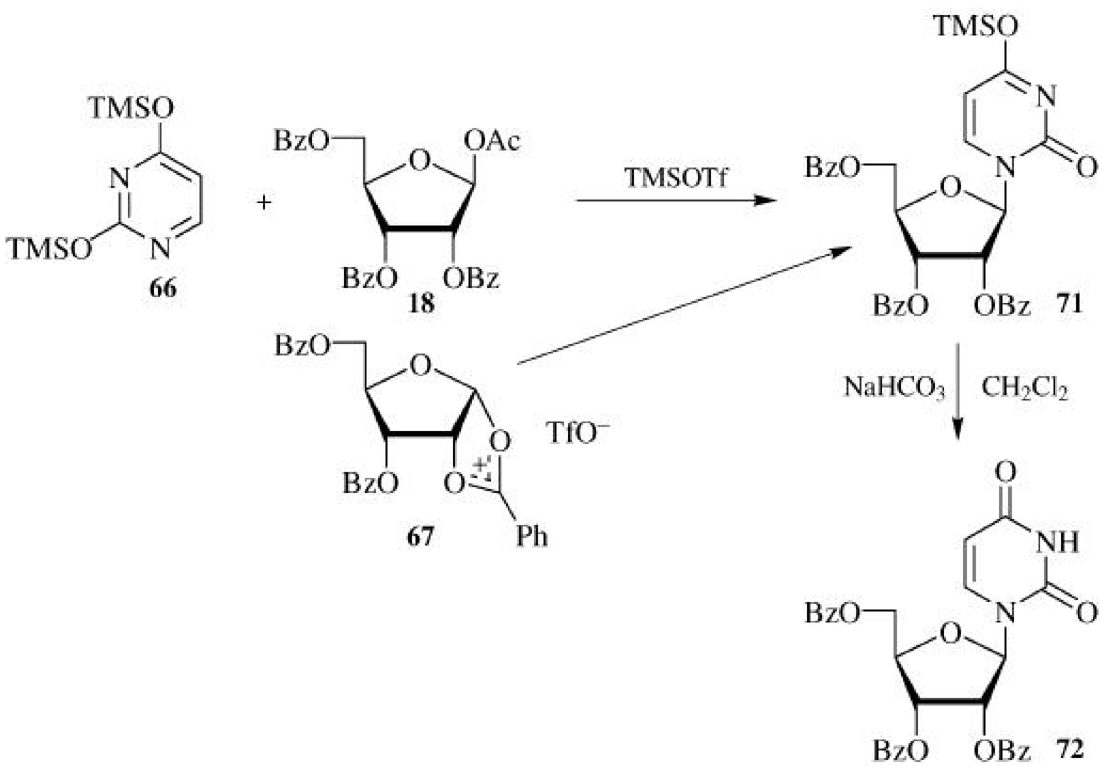
During the total synthesis of 5-methylaminomethyl-2-thiouridine, (125, 126) a rare nucleoside from tRNA, (127) the silylated 2-thiouracil **100** was reacted with 1-chlorosugar **19** in the presence of $AgClO_4$ in benzene to give the substituted 2-thiouridine **101**, in which the *N*-*tert*-butoxycarbonyl group had been lost. The only strong Lewis acid that could have cleaved the BOC group was $TMSClO_4$ (**70**), whose formation as an intermediate during the Silyl-Hilbert-Johnson reaction in the presence of $AgClO_4$ had been postulated previously. (74, 80) It was subsequently demonstrated that $TMSClO_4$, as well as TMSOTf, does indeed cleave *N*-BOC groups in amino acids and peptides. (128-130)



$TMSClO_4$ and TMSOTf had previously been investigated using ^{29}Si NMR. (131) These studies showed that they are much stronger Lewis acids than, for example, $(TMS)_2SO_4$ or TMSCl. Whereas the explosive (82) $TMSClO_4$ is prepared from $AgClO_4$ and TMSCl in benzene, the chemically stable TMSOTf (**102**, bp 133–134°) is obtained by heating TfOH with TMSCl. (131) The higher boiling TMS nonaflate (**103**, bp 68–69°/11 torr) is formed on heating nonaflic acid with TMSCl or on reacting potassium nonaflate with TMSCl.



Since Friedel-Crafts catalysts such as $SnCl_4$ or $TiCl_4$ had been used successfully for the Silyl-Hilbert-Johnson nucleoside synthesis, (84) these new silylated Lewis acids $TMSClO_4$ and TMSOTf were reacted with silylated uracil **66** and **18**. It was found that catalytic amounts of $TMSClO_4$ or TMSOTf in 1,2-dichloroethane or acetonitrile were adequate for generating the reactive intermediate cation **67**, although the use of 1.1 equivalents was more efficient. Reaction of **67** with silylated uracil **66** leads to the silylated intermediate **71** and regenerated $TMSClO_4$ or TMSOTf. (132, 133) Hydrolysis with aqueous $NaHCO_3$ in CH_2Cl_2 affords 2′,3′,5′-tri-*O*-benzoyluridine (**72**) in more than 80% yield. Most importantly, during hydrolysis no emulsions are formed (132, 133) as are usually encountered on aqueous workup employing $SnCl_4$ as catalyst for nucleoside synthesis.



In contrast to $TMSClO_4$ and TMSOTf, the weaker Lewis acids (131) $(TMS)_2SO_4$ and TMSCl do not promote nucleoside formation, since they apparently do not convert **18** into the sugar cation **67**. However, the even weaker Lewis acid TMSI, which can be prepared in situ from TMSCl and NaI in acetonitrile, (134) does catalyze the formation of nucleosides; TMSI is a combination of the hard trimethylsilyl cation and the soft iodide anion and effects nucleoside synthesis via an apparent push and pull mechanism. (135–139,139a,c,d),On reaction of 1-*O*-acetyl-5-*O*-pivaloyl-(3*S*)-2,3-dideoxyapiose with silylated thymine or

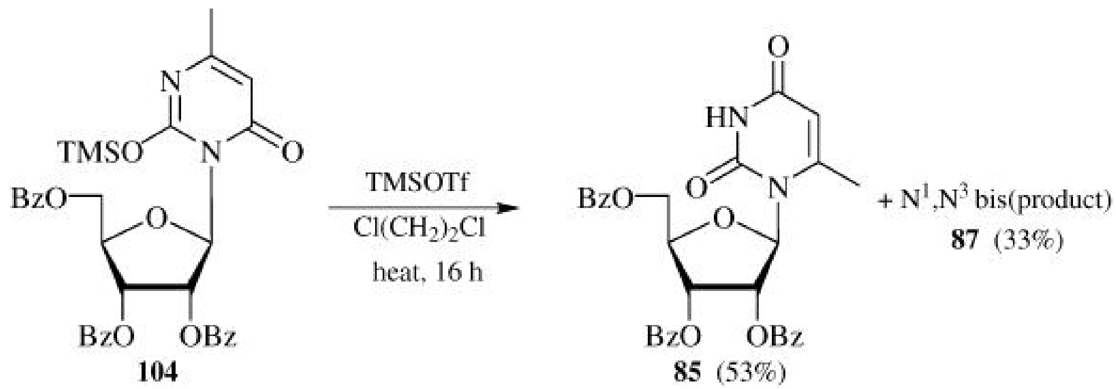
N^6-benzoyladenine in acetonitrile at – 5 to 0°, catalytic amounts of TMSI at – 5° seem to induce faster formation of the mixture of *syn* and *anti* nucleosides than equivalent amounts of TMSOTf at – 5°. (139a) Pure TMSI is, however, quite unstable and thus must always be redistilled before use; it will also cleave ester or ether functionalities in the sugar or heterocyclic moieties.

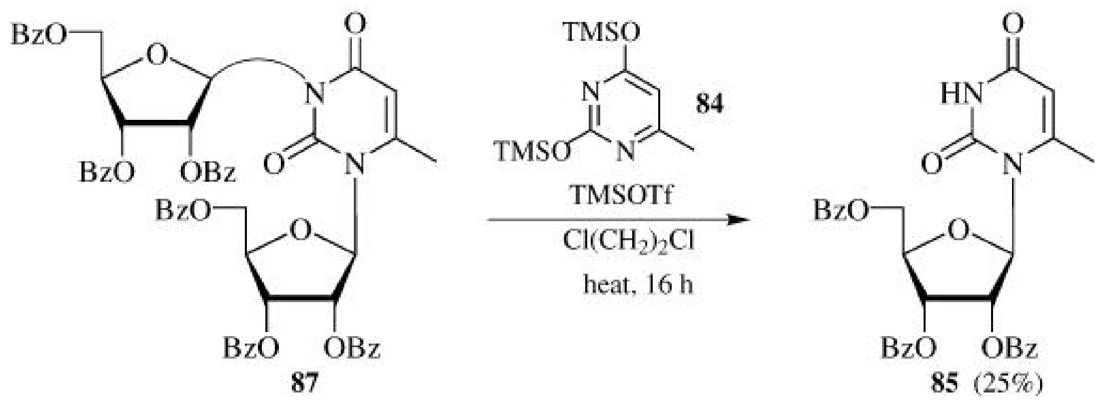
The persilylated polymeric perfluorinated sulfonic acid Nafion® (139b) has not as yet been explored as catalyst, (133) although it could be recovered by filtration and regenerated by heating with excess TMSCl.

Importantly, use of TMSOTf (**102**) as catalyst dramatically increases the yields of the 5-methoxy- or 5-morpholino-2,3,5-uridine tri-*O*-benzoates (**81b** and **81c**) from the silylated uracils **80b,c** and **18**. Thus, even in 1,2-dichloroethane, 89% of **81b** (compared to 53% using $SnCl_4$) and 95% of **81c** (compared to 39% using $SnCl_4$) are obtained. Analogously, use of catalytic TMSOTf with the rather basic silylated 4-tri methylsilyloxypyridine (**92a**) and 4-trimethylsilylaminopyridine (**92b**) gives the corresponding nucleosides **93a** and **93b** in 87% and 80% yields, (133) whereas **93a** is obtained only in 63% yield with $SnCl_4$. (99) For the explanation of these differences in chemical behavior see the following section.

Under carefully controlled conditions using TMSOTf in purified acetonitrile, silylated 6-methyluracil **84** affords the desired protected 6-methyluridine **85** in 71% yield compared to 41% with $SnCl_4$. (133) Furthermore, the undesired acylated N^3-nucleoside **86** rearranges on silylation to **104**, and heating with TMSOTf to yield 53% of the protected N^1-nucleoside **85** and 33% of the N^1,N^3-bis(riboside) **87**. The sterically hindered **87** reacts on heating with silylated 6-methyluracil **84** and TMSOTf to give the N^1-nucleoside **85**. (133)

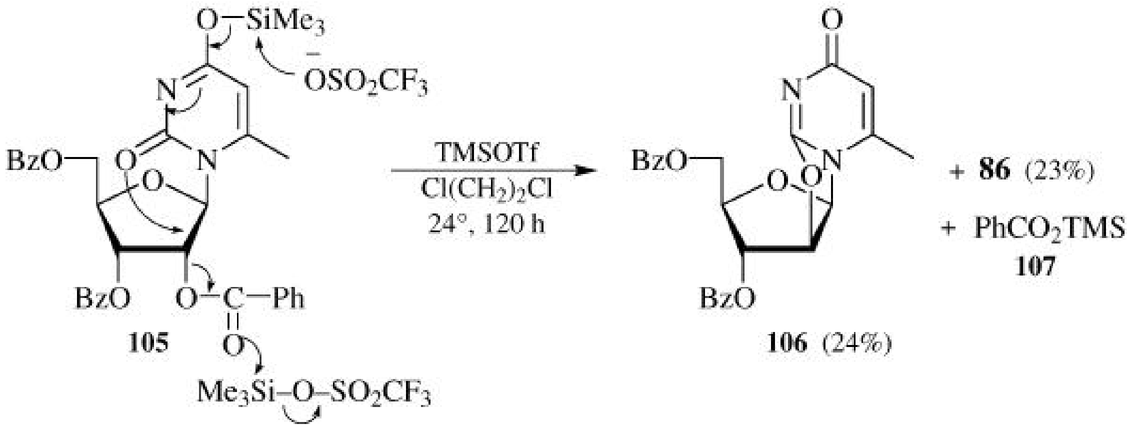
On extended exposure of silylated 2′,3′,5′-tri-*O*-benzoyl-6-methyluridine **105** to TMSOTf in 1,2-dichlorethane, 24% of the benzoylated 2,2 -anhydronucleoside **106** is formed together with 23% of the N^1,N^3-bis(riboside) **86** and trimethylsilyl benzoate. (133) This cyclization to **106** might be favored by the *syn* conformation of **85** and **105**.





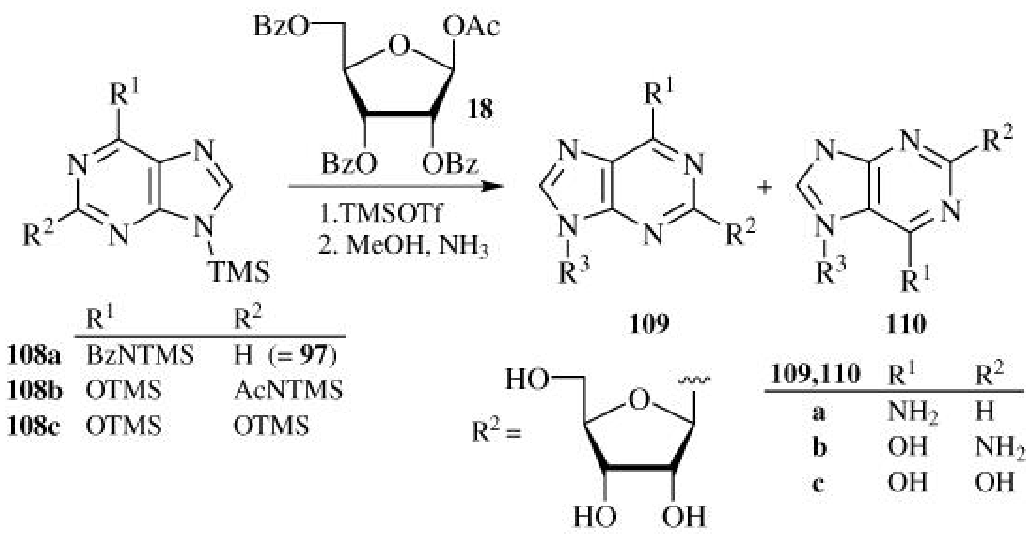
Silylated *N*^{6}-benzoyladenine **108a**, as well as silylated *N*^{2}-acetylguanine **108b** and xanthine **108c**, afford after saponification the corresponding crystalline purine nucleosides **109a–c** in 81, 66, and 49% yields, respectively. (133)

Following the TMSOTf catalyzed synthesis of *N*^{6}-benzoyladenosine-2′,3′,5′-tri-*O*-benzoate by TLC indicates that the reaction proceeds at least partially via the protected *N*^{3}-**38** or *N*^{7}-nucleoside **110a** to give adenosine after saponification.

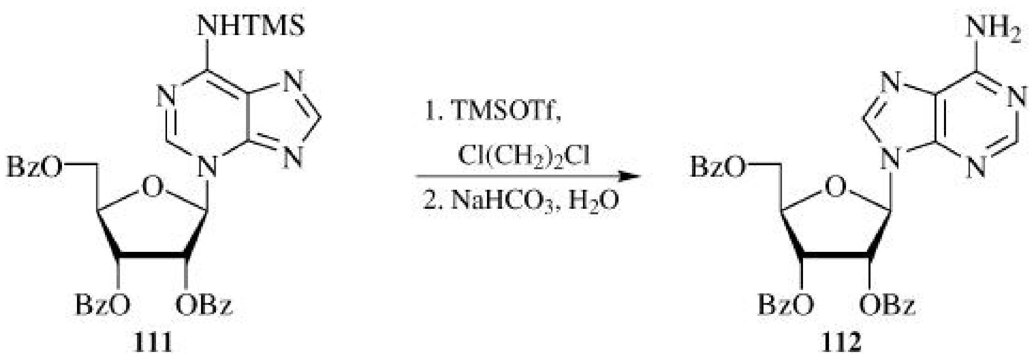


Thus the N^6-silylated N^3-adenosine **111** is smoothly rearranged in the presence of TMSOTf to 2′,3′,5′-tri-*O*-benzoyladenosine (**112**). (133)

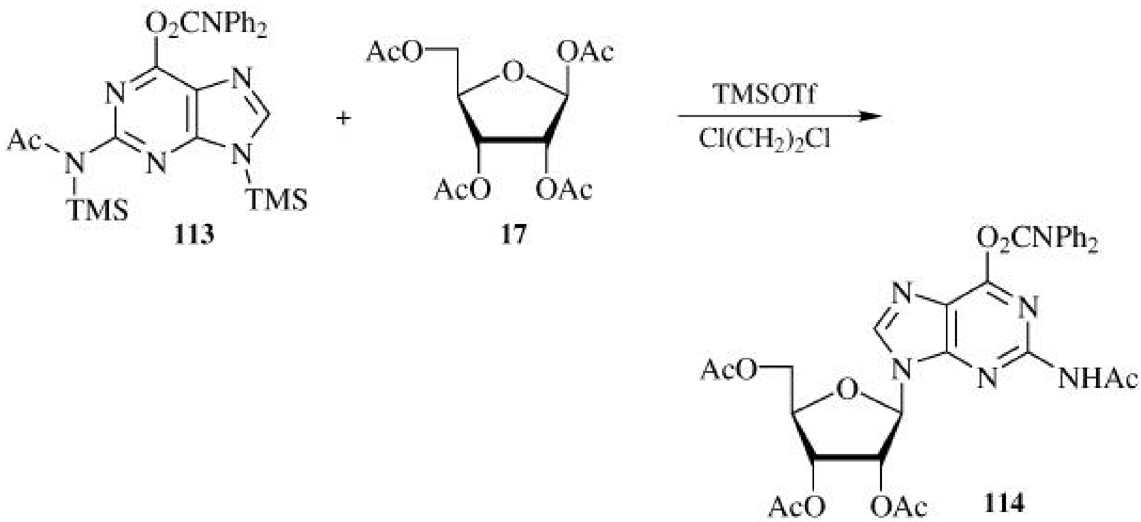
The reaction of silylated N^2-acetylguanine (**108b**) with riboside **18** in the presence of TMSOTf at reflux in 1,2-dichlorethane affords, after workup and saponification of the protecting groups with methanolic ammonia, an overall yield of 66% of crystalline guanosine containing at most traces of the N^7-isomer **110b** (133) and not, as later claimed, a crystalline mixture of **109b** and **110b**. (140-141a) The guanosine synthesis apparently proceeds at least partially via the corresponding N^7-nucleoside, which can be isolated after saponification as the unprotected nucleoside **110b** along with the desired thermodynamically controlled **109b**. Heating of the reaction mixture with TMSOTf in boiling 1,2-dichloroethane affords a mixture of the protected N^7- and N^9-guanosines in which only 10–15% of the N^7-nucleoside can be detected, whereas use of $SnCl_4$ in acetonitrile results in predominant formation of the protected N^7-nucleosides. (142) These results seem to indicate that in 1,2-dichloroethane or acetonitrile, $SnCl_4$ forms a σ or chelate complex with the N^3- and N^9-nitrogen atoms of silylated N^2-acetylguanine, blocking the access of **67** to N^9 or the rearrangement of the silylated N^7-guanosine to the N^9-guanosine. However, reaction of **108b** with **17** in the presence of TMSOTf



in 1,2-dichloroethane at reflux affords, after saponification, the N^9- and N^7-guanosines **109b** and **110b** in a ratio of 2:1. The sugar derivative **18**, which is converted into the more stable sugar cation **67** compared with **27** (p. 6) and will thus facilitate any rearrangement of the protected and silylated N^7-nucleoside into the corresponding N^9-nucleoside, furnishes **109b** and **110b** in a ratio of 6:1 under the same reaction conditions (cf p. 48). (142)

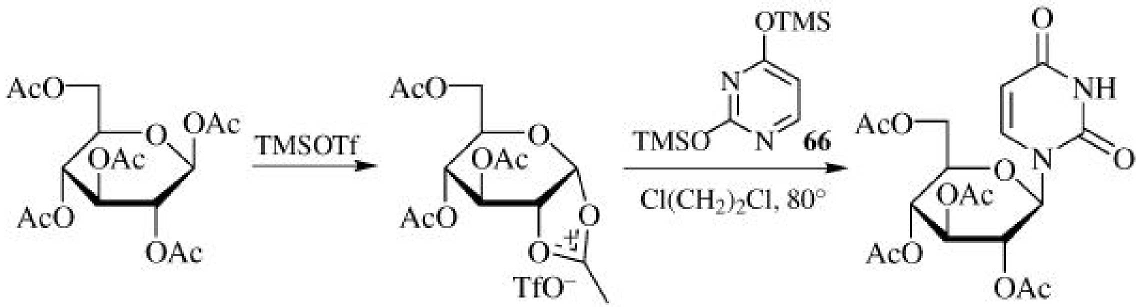


Blocking the 6-oxygen in N^2-acetylguanine with the bulky diphenylcarbamoyl group followed by silylation to **113** and subsequent reaction with **17** in the presence of TMSOTf leads to the protected guanosine **114**, which can be saponified to the natural guanosine **109b** in 68% overall yield. (140) Analogously, in the TMSOTf catalyzed reaction with **17**, introduction of a 6-(4-nitrophenylethoxy) group into 2-bromoxanthine followed by silylation gives less than 5% of the undesired N^7-nucleoside. (143) Reaction of **113** with 1,2,3,4,6-penta-*O*-acetyl- β-D-galactopyranose in the presence of TMSOTf in toluene at 80° gives, in addition to the anticipated protected N^9-nucleoside, a rearranged protected nucleoside in which the O^6-diphenylcarbamoyl group has migrated to replace the N^2-acetyl group. (143)

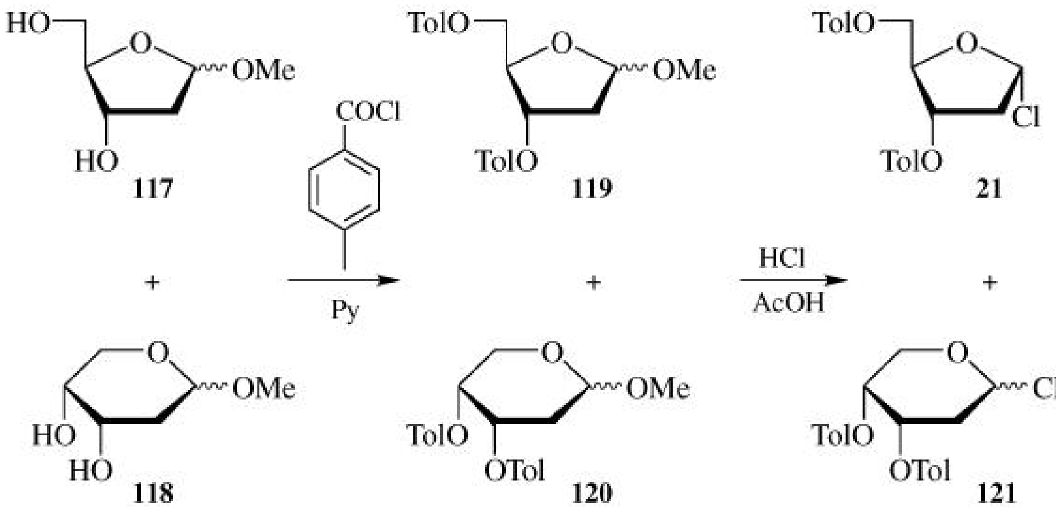


However, in view of the additional steps involved in preparing O^6-blocked guanine derivatives, the direct synthesis of guanosine (or analogs) starting with **108b** (or similar bases) and **18** to give crystalline guanosine in 66% yield (133) after saponification should always be considered. The synthesis of 9-substituted guanines has been reviewed. (144)

Peracylated pyranose **23** is transformed on heating with TMSOTf into the reactive pyranose cation **115**, which combines with silylated uracil **66** to give 1-[2 ,3 ,4 ,6 -tetra-*O*-acetyl- β -D-glucopyranosyl]uracil (**116**) in 89% yield. (133) The lower reactivity of pyranose derivatives with TMSOTf permits differentiation between the furanose and pyranose forms. Brief treatment of 2-deoxyribose with absolute methanol-HCl gives primarily the two kinetically controlled 1-*O*-methyl-2-deoxyribofuranoses (**117**) and minimal amounts of the 1-*O*-methylpyranoses (**118**), which as the thermodynamically controlled products become the major products on longer exposure to methanolic HCl. (145)



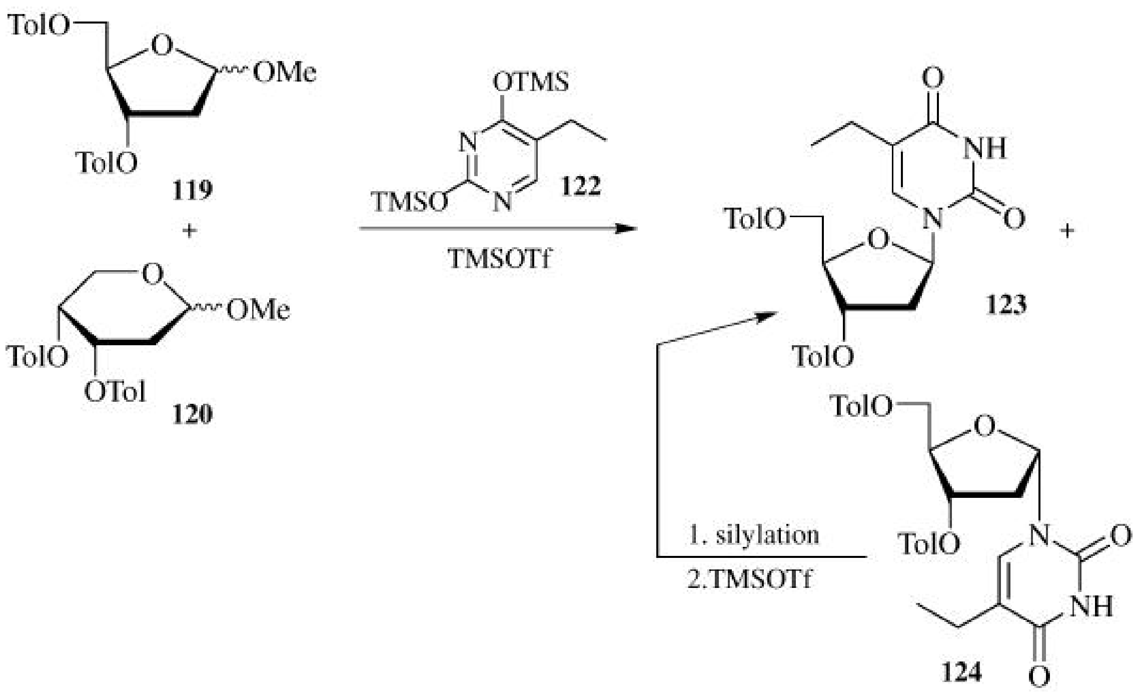
23 **115** **116** (89%)



Acylation of the mixture of **117** and **118** with *p*-toluolyl chloride and pyridine affords mainly a mixture of the two anomeric *O*-acylated furanoses **119** and a minor amount of the anomeric pyranoses **120**, which can be readily separated by chromatography on silica gel with hexane-diisopropyl ether. (146) This mixture of the acylated furanoses and pyranoses is commonly treated with anhydrous HCl in acetic acid to give the labile crystalline **21** on crystallization as well as some noncrystalline **121**. (51) The crystalline **21** has become the standard sugar for the preparation of 2 -deoxynucleosides since the 3′,5′-bis(*p*-toluoyl) β -nucleosides usually have higher melting points and lower solubility than the corresponding α -nucleosides, often permitting their separation by crystallization.

Because formation of the anomeric acylated *O*-methylfuranosides **119** is kinetically controlled, they are more readily converted to the corresponding reactive furanose cation intermediates by TMSOTf than the anomeric acylated 1-*O*-methylpyranosides **120**. Thus a mixture of **119** and **120** reacts with silylated 5-ethyluracil **122** at ambient temperature to give 58% of the desired β

-nucleoside **123** as well as 31% of the undesired α -nucleoside **124**. The same mixture of **119** and **120** affords only 35% of the crystalline protected **21** (133) on treatment with HCl-AcOH. Because of the reversibility of nucleoside synthesis, an undesired 2′-deoxy- α -nucleoside such as **124**, when silylated and kept for 46 hours at 24° with TMSOTf, affords 27% of the desired β -nucleoside **123** as well as 67% of recovered α -nucleoside **124**. (133)



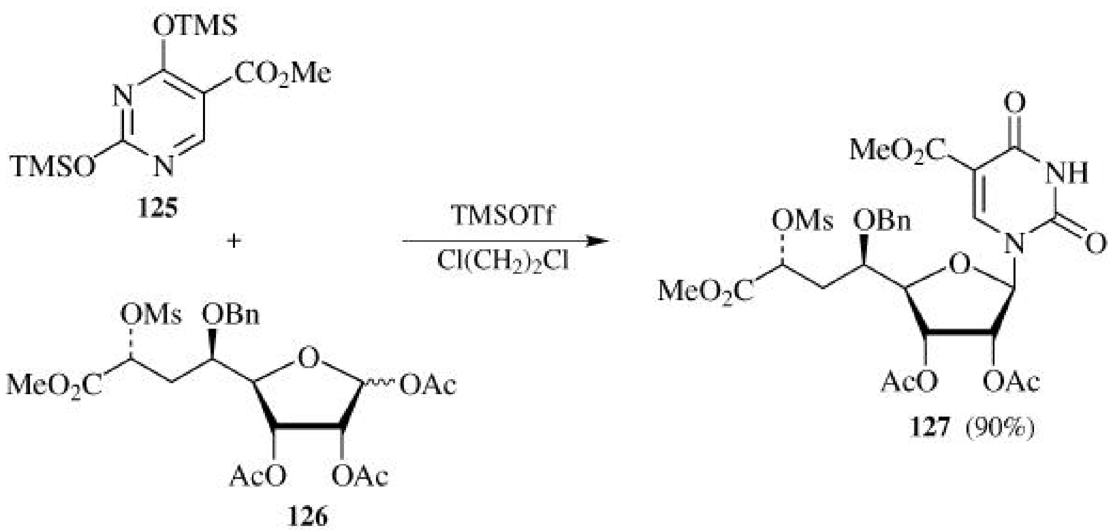
A mixture of **119** and **120** was subsequently utilized to prepare analogously 2 -deoxynucleosides of silylated 2-(1*H*)pyrimidone. (147) Related mixtures of 2-deoxyfuranosides and pyranosides were reacted with silylated uracil (148) and silylated 5-iodopyrimidin-2-one. (149)

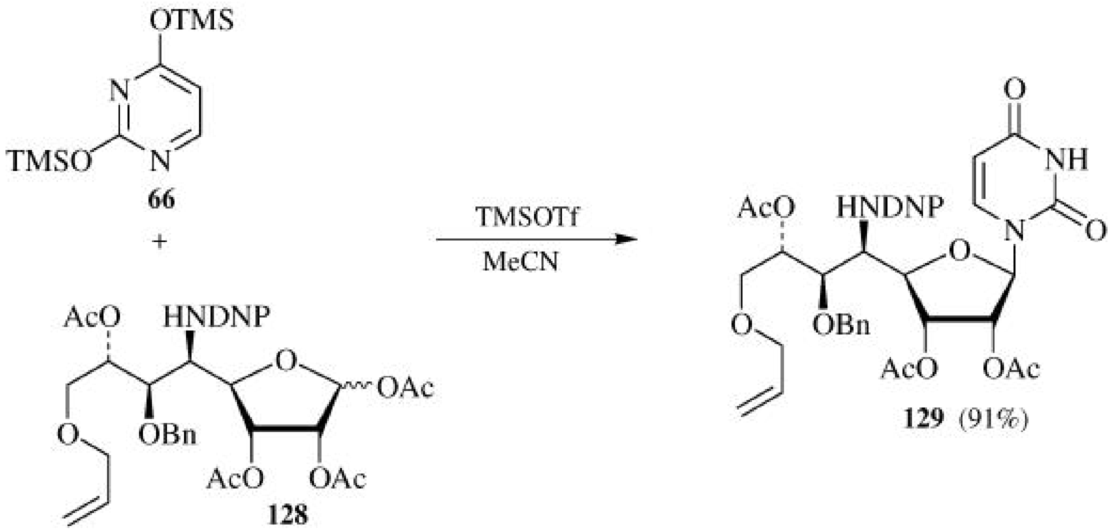
Although longer reaction times increase the amount of β -anomer **123** obtained from **124**, they also lead to gradual decomposition of the sensitive 2-deoxyribose moiety in **123** and **124** to give 2-toluoyloxymethylfuran **259** (see section on 2 -deoxynucleosides). (150) Since there is always an equilibrium between the activated protected β - and α -anomers, silylation of β -anomers such as 3′,5′-di-*O*-acetyl-*N*^{4}-benzoyl-2 -deoxycytidine with *N,O*-bis(silylacetamide) (BSA), and subsequent heating with TMSOTf in acetonitrile for 3 hours at 80° affords 51% of the corresponding protected α -anomer. (151-151a) Treatment of 3 ,5 -di-*O*-acetylthymidine with acetic anhydride and sulfuric acid leads to the predominant formation of the 3′,5′-di-*O*-acetyl- α -thymidine. (152-152a) On the other hand, free or

3 ,5 -*O*-protected thymidines are cleaved to glycals on heating with HMDS and $(NH_4)_2SO_4$. (152b-152c)

On employing 1-*O*-methyl-3,5-di-*O*-toluoyl-2-deoxyribofuranoside **119** or 1-*O*-methyl-2,3,5-tri-*O*-benzoyl-d-arabinofuranoside **328** and insufficient amounts of TMSOTf or $SnCl_4$, seconucleosides such as **332** (which are probably derived via activated intermediates such as **333**) can be isolated (cf the section on arabinonucleosides). These seconucleosides undergo cyclization to the anticipated nucleosides upon introduction of additional amounts of catalyst.

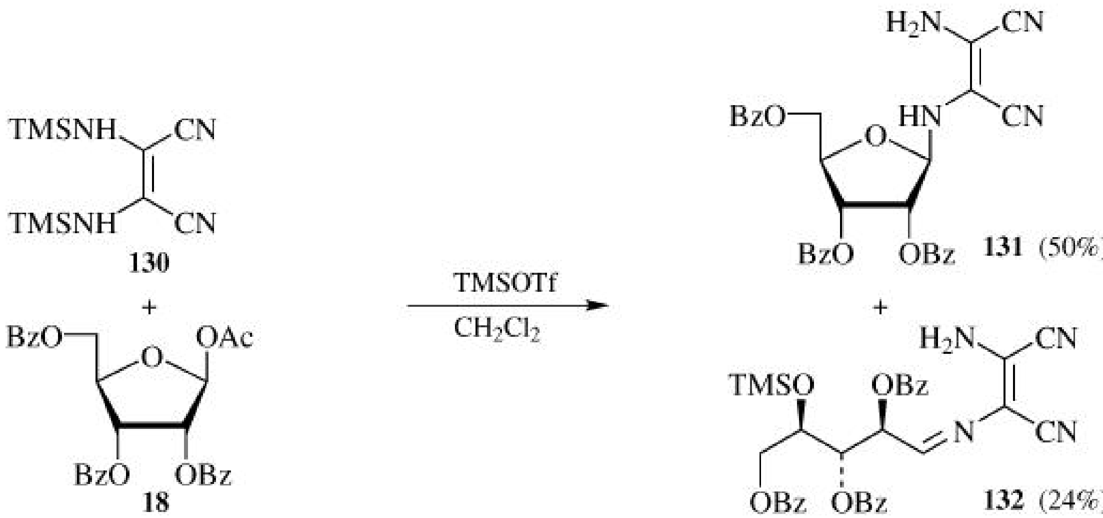
Sugar moieties containing sensitive azide groups (153, 279) as well as an assembly of complex functional groups have been employed. In the synthesis of octosyl acid A, silylated 5-carbomethoxyuracil **125** is reacted with the sugar moiety **126** to give the nucleoside intermediate **127** (154, 155) in 90% yield (see a related approach to octosyl acid A (156)). Analogously, the reaction of silylated uracil **66** with the rather complex sugar moiety **128** yields intermediate **129** (91%) for the synthesis of ezomycin (157) (see a related approach to ezomycin A (158)). In the synthesis of hikizimycin, an even more complex sugar moiety was employed with TMSOTf in nitrobenzene at 127° (see **515** →**516**). (159, 160) The synthesis of nucleoside antibiotics was reviewed recently. (160a)

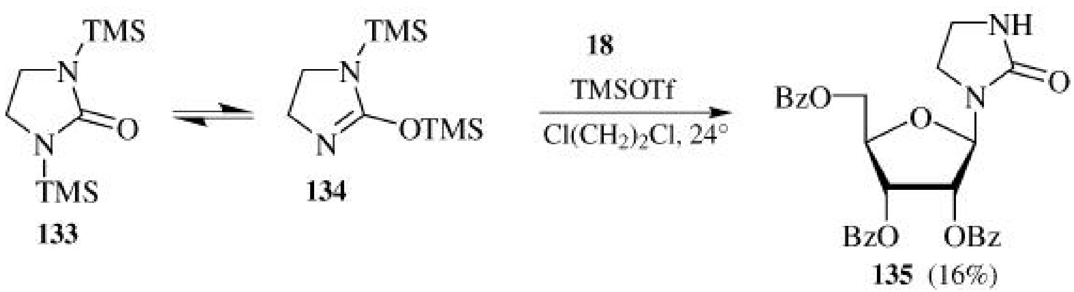




On reacting complex sugar moieties containing many basic functional groups, one has to realize that all these groups form either weak σ complexes with TMSOTf or stronger chelate-type complexes with $SnCl_4$, $TiCl_4$, or Et_2AlCl, which will slow down and perhaps even alter the course of the reaction. Thus, use of additional amounts of catalyst is necessary.

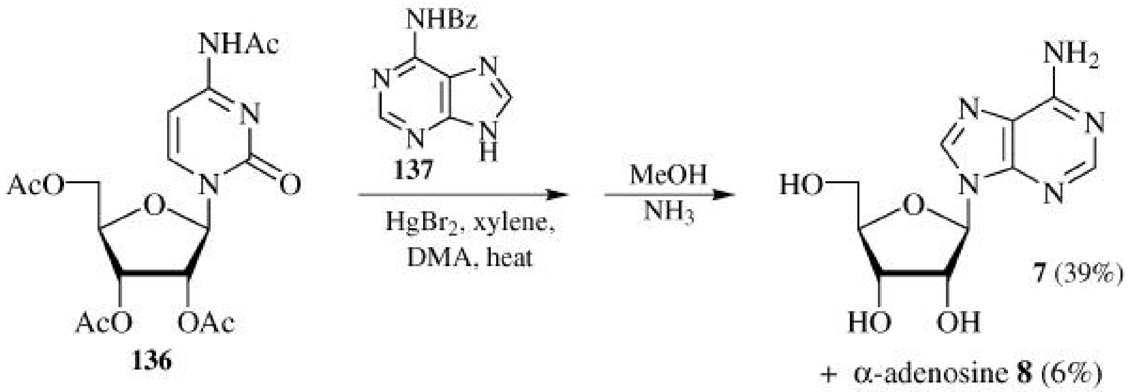
Even very weakly basic systems can be silylated and converted into nucleoside-type structures. Thus 2,3-diaminomaleonitrile (DAMN) reacts in its disilylated form **130** with **18** and 2 equivalents of TMSOTf in CH_2Cl_2 to furnish 50% of nucleoside **131** and 24% of the seconucleoside **132**, whereas the same reaction in the presence of only 1 equivalent of TMSOTf gives only imine **132**. (161) Similarly, the silylated cyclic urea **133** or **134** affords only 16% of nucleoside **135** with **18** and TMSOTf as catalyst. (162) This low yield, however, might be due to the presence of monosilylated or free trifluoroacetamide derived from bis(trimethylsilyl)trifluoroacetamide (BSTFA) used for the silylation of the cyclic urea to **133** or **134**, since the trifluoroacetamide or its monosilyl derivative can compete with **133** → **134** for the reactive sugar intermediate **67**. This possibility was recently confirmed in the silylation of 1,2,4,6-thiatriazin-3-one-1,1-dioxides with BSA followed by reaction with peracylated sugars in the presence of TMSOTf in acetonitrile at reflux, where only moderate yields of protected nucleosides were obtained, along with up to 46% of 1- β -acetamides of the protected sugars. (162a)



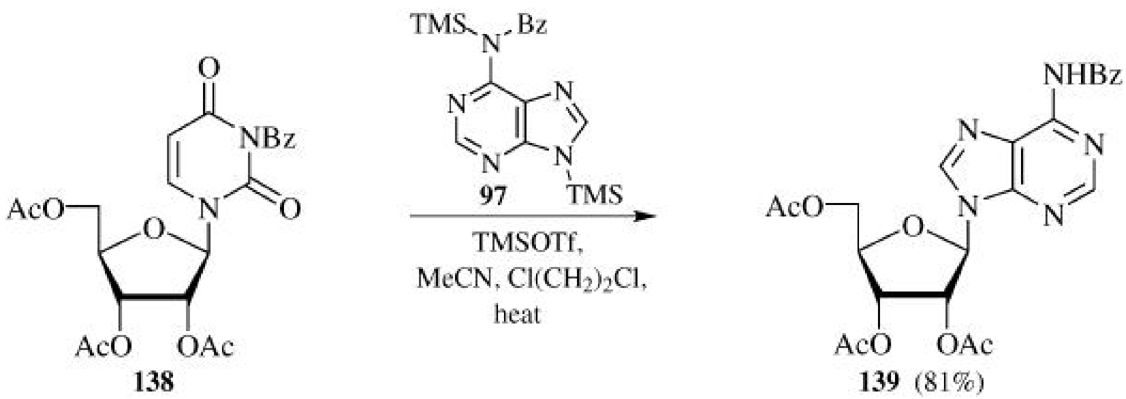


4.3. Transglycosylation with Lewis Acids

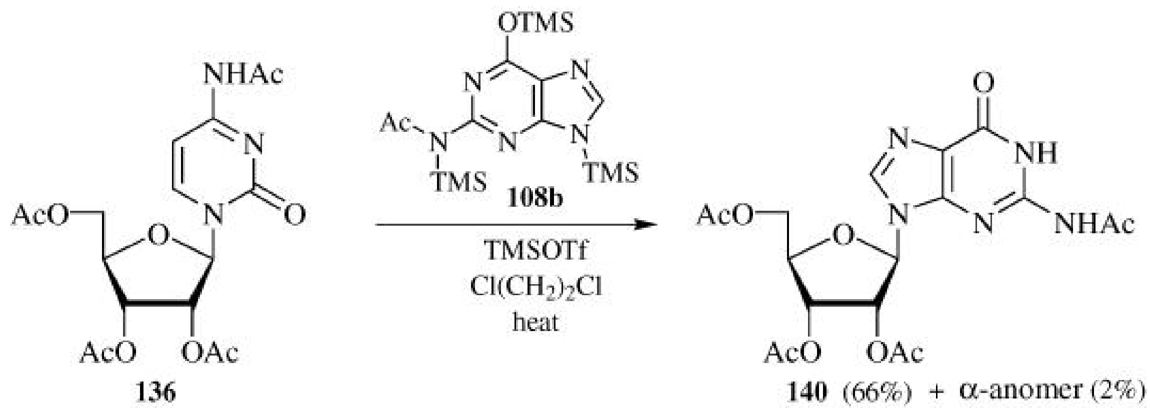
Since nucleoside formation in the presence of Lewis acids is a reversible process, a nucleoside base in a given nucleoside can be exchanged for another nucleoside base. This was first investigated by treating peracylated cytidine **136** with *N*[6]-benzoyladenine (**137**) in the presence of $HgBr_2$ and DMA in xylene at reflux to afford after saponification 39% adenosine (**7**) and 6% α -adenosine (**8**). (163) An exchange of ribose in 2 ,3 -isopropylideneinosine by acetobromoglucose gives the corresponding inosine analog in moderate yield. (164)



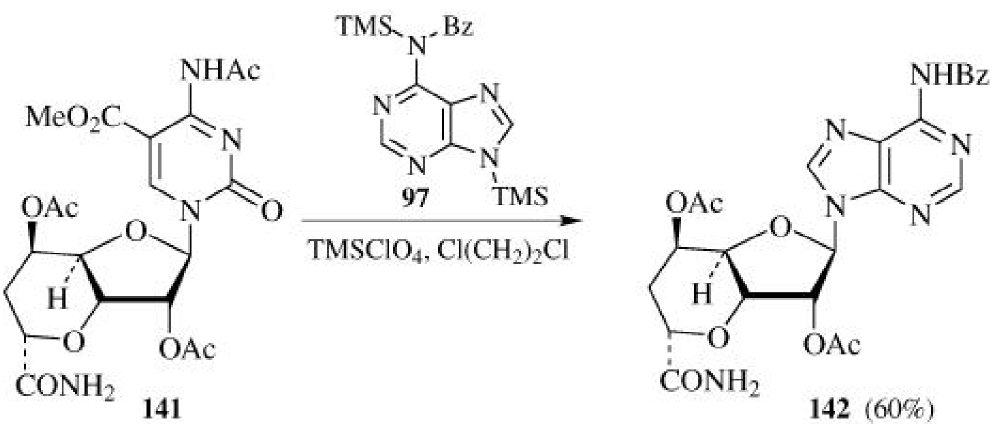
Much more effective are transglycosylations of silylated nucleosides and bases in the presence of trimethylsilyl perchlorate or TMSOTf. (151,165–168,170–172,176–179) N^3-Benzoyl-2 ,3 ,5 -tri-*O*-acetyluridine (**138**) and excess persilylated N^6-benzoyladenine (**97**) furnish an 81% yield of N^6-benzoyl-2 ,3 ,5 -tri-*O*-acetyladenosine (**139**), whereas $SnCl_4$ as catalyst gives a much lower yield of a mixture of protected β - and α -adenosine. (166) N^4-2 ,3 ,5 -Tetraacetylcytidine (**136**) and persilylated N^2-acetylguanine **108b** afford peracetylated guanosine **140** in 66% yield as well as 2% of the corresponding α -anomer in the presence of TMSOTf. (166)

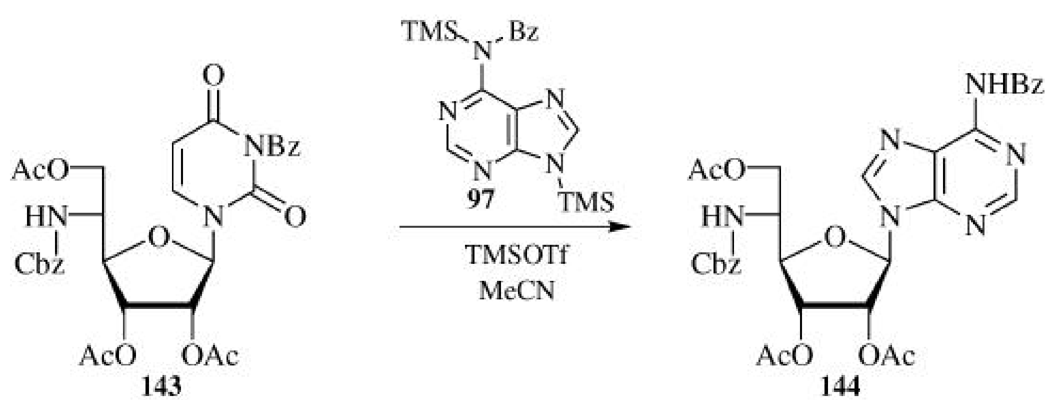


A derivative of octosyl acid, **141**, reacts with **97** in boiling 1,2-dichloroethane to give analog **142** in 60% yield. (165, 166) Similarly, the transformation of the polyoxin derivative **143** affords **144**. (167) A similar transglycosylation of a complex



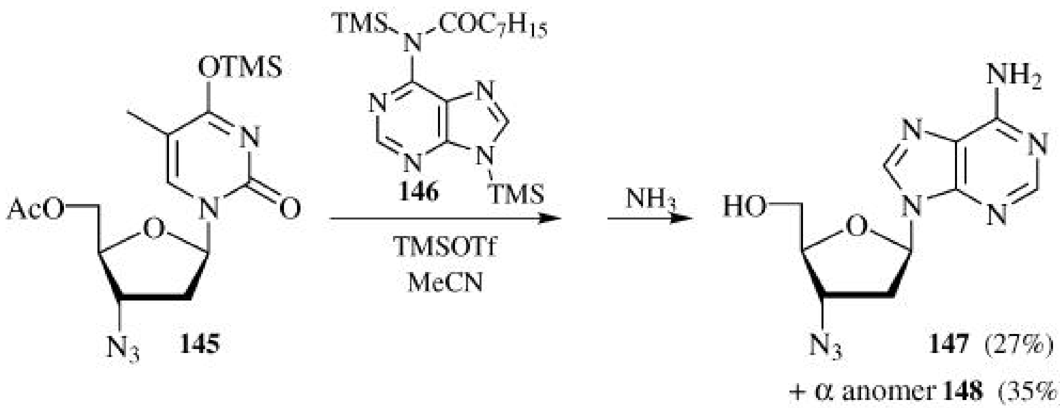
uridine derivative leads to the corresponding adenosine derivative as an approach to a total synthesis of sinefugin (168) (see also the transglycosylation of protected griseolic acid (169)).



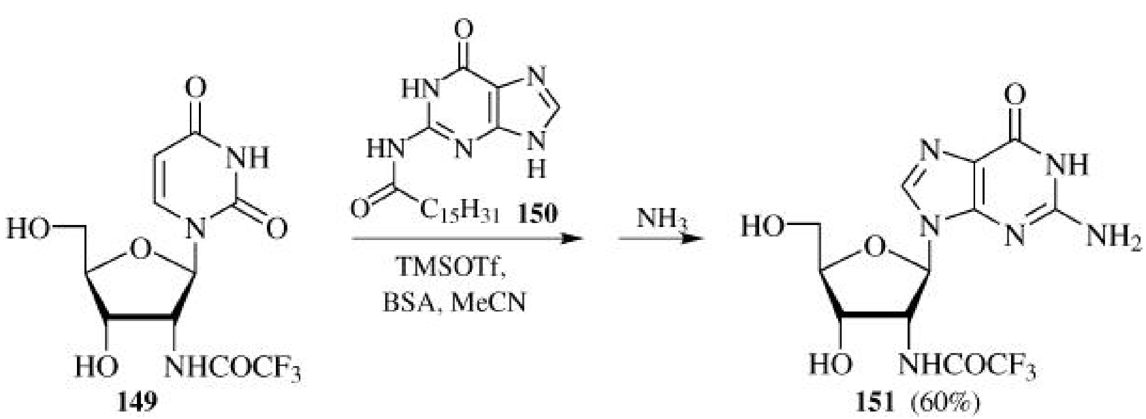


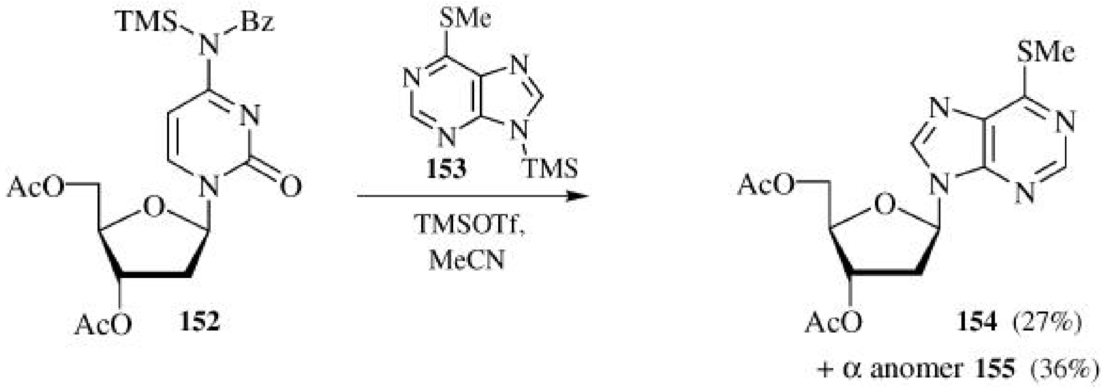
Reaction of persilylated 3′-azido-2′-deoxy-5′-*O*-acetylthymidine (**145**) with silylated N^6-octanoyladenine (**146**) affords after saponification 27% of the corresponding β -purine nucleoside **147** as well as 35% of the corresponding α -anomer **148**. (170) Reaction with persilylated N^2-palmitoylguanine gives 28% of the corresponding β -N^9-guanine nucleoside. (170)

The analogous reaction with silylated 2,6-diacetamidopurine affords the corresponding 2-aminoadenosine derivative. (171) Transformations of persilylated 3′-deoxy-3′-fluorothymidine and its 5′-acetyl derivative with persilylated N^2-acylguanine, (172, 173) 2-fluoroadenine, (174) N^6-benzoyladenine, (175) and benzimidazole (176) as well as of uracil and of 5-substituted uracils, (177, 178) furnish the corresponding protected β -2′-deoxynucleosides together with α -anomers in moderate yields.



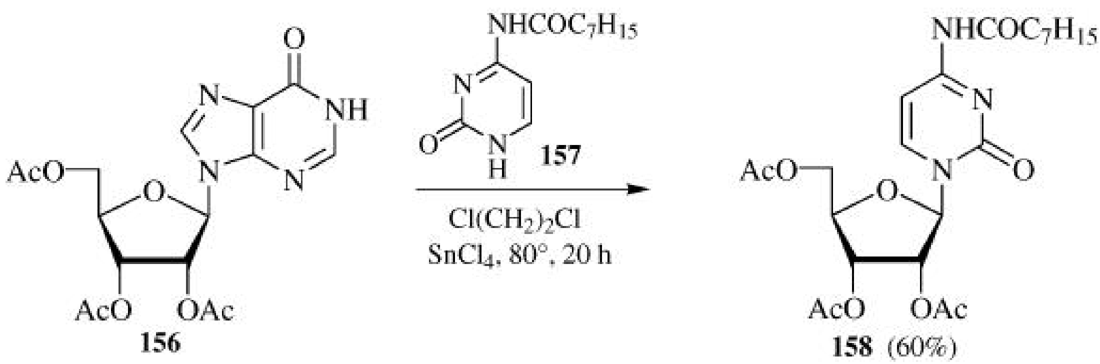
The transglycosylation of 2′-deoxy-2′-trifluoroacetylaminouridine (**149**) with N^2-palmitoylguanine **150** in the presence of BSA and TMSOTf and subsequent saponification with NH_3 affords guanine nucleoside **151** in 60% yield, (179) whereas **152** and **153** react in the presence of BSA and TMSOTf to give a 27% yield of **154** and 36% of the corresponding α -anomer **155**. (151)

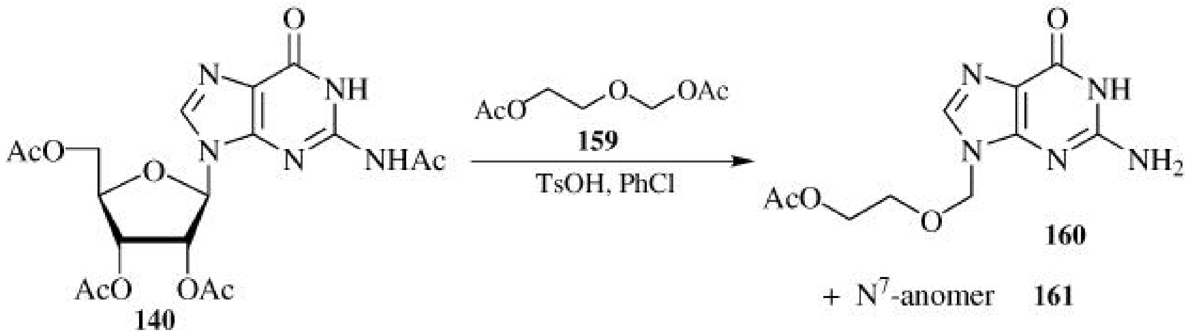




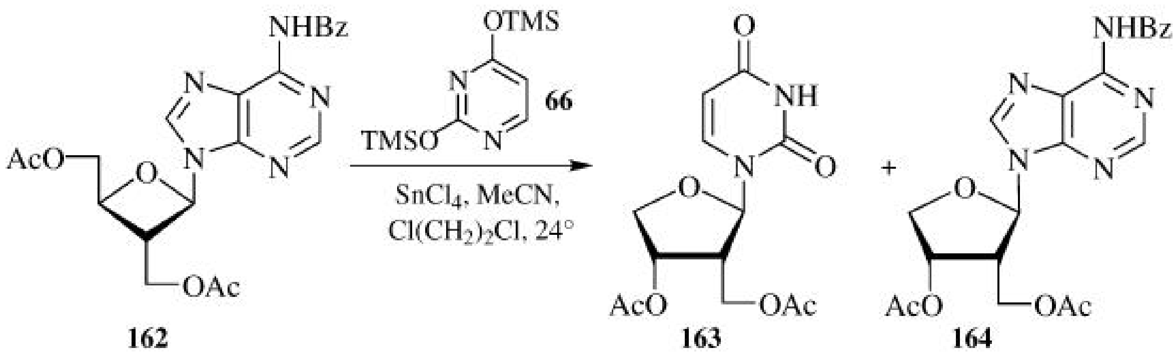
Purine nucleosides can also be transformed into the corresponding pyrimidine nucleosides. Thus, protected purine nucleosides such as **156** and N^4-octanoyl cytosine (**157**) on heating with BSA and $SnCl_4$ in 1,2-dichloroethane provide the corresponding cytidines **158** in 30–60% yield. (180)

Likewise N^2-2′,3′,5′-tetraacetyl guanosine (**140**) reacts with 2-acetoxyethyl acetoxymethyl ether (**159**) in chlorobenzene at reflux in the presence of traces of *p*-toluenesulfonic acid to furnish the desired N^9-derivative **160** as well as the N^7-analog **161** in a 9:7 ratio. (181, 182)





On attempted transglycosylation of N^6-benzoyloxetanocin di-*O*-acetate (**162**) with persilylated uracil **66** in the presence of $SnCl_4$, the intermediate sugar cation rearranges to form furanose nucleosides **163** and **164**. (183) For further examples of transglycosylation, see Refs. 184-186. For a review of transglycosylation of purine nucleosides, see Ref. (186a).



4.4. One Step–One Pot Nucleoside Syntheses

Since silylations are accelerated by Lewis acids, (187) and the silylation of heterocyclic bases is much more rapid in the presence of Friedel-Crafts catalysts, one can combine the different steps of nucleoside synthesis in a one step–one pot procedure in a polar solvent such as acetonitrile. (188, 189) (a) silylation of the heterocyclic base, (b) silylation of the triflate or nonaflate salts to form TMSOTf or ($(CH_3)_3SiOSO_2(CF_2)_3CF_3$ (if $SnCl_4$ is not used as a catalyst), and (c) nucleoside synthesis with acylated 1-*O*-acyl- or 1-*O*-alkylsugars in the presence of a Friedel-Crafts catalyst.

Such a one step–one pot preparation avoids the handling of the easily hydrolyzed silyl compounds and saves time since no prior silylation step is needed. Under these one step–one pot conditions the amounts of TMSCl and HMDS have to be chosen in such a way that all reactive heterocyclic hydroxy, thio, amino, or amido groups as well as the free triflate or nonaflate acids $C_nF_{2n+1}SO_3H$ or their alkali salts are silylated with formation of NH_4Cl and NaCl or KCl, since any free NH_3 would neutralize the Friedel-Crafts catalyst. Because all these salts are practically insoluble in acetonitrile, they precipitate and the equilibria are shifted toward the desired electrophilic silyl ester. (189)

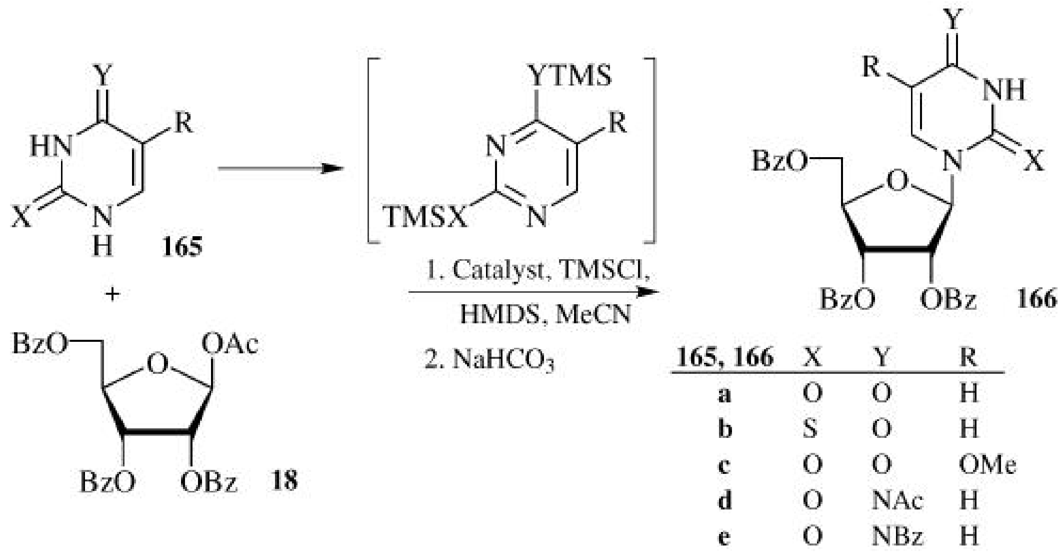
$$3\ \mathrm{TfOH} + \mathrm{HMDS} + \mathrm{TMSCl} \longrightarrow 3\ \mathrm{TMSOTf} + \mathrm{NH_4Cl}$$

$$n\text{-}\mathrm{C_4F_9SO_3K} + \mathrm{TMSCl} \longrightarrow \underset{\mathbf{103}}{\mathrm{TMSOSO_2C_4F_9}\text{-}n} + \mathrm{KCl}$$

Since potassium nonaflate ($C_4F_9SO_3K$) is only partially soluble in boiling acetonitrile, the KCl formed on its reaction with TMSCl to give **103** could occlude unreacted reagent. Therefore, an excess of finely powdered potassium nonaflate should be employed.

As described in Eq. 1, a mixture of 0.33–0.40 equivalent of TMSCl and HMDS has to be used for free TfOH, whereas for potassium nonaflate (Eq. 2) equimolar amounts of TMSCl have to be employed. (189)

For silylating uracil , cytosine, or a purine such as N^6-benzoyladenine containing two reactive oxygen or oxygen and nitrogen functionalities, a mixture of at least 0.7–0.8 equivalent each of TMSCl and HMDS is necessary to obtain the corresponding persilylated uracil , cytosine, or N^6-benzoyladenine with concomitant formation of 0.7–0.8 equivalent of NH_4Cl . For a heterocyclic base such as 4-pyridone with only one reactive oxygen group, only ca. 0.4 equivalents each of TMSCl and HMDS are needed to afford the silylated base **92a** (X = O). Uridine-2 ,3 ,5 -tri-*O*-benzoate (**166a** = **72**) is readily obtained in 80–84% yield starting from uracil (**165a**) and **18** employing free triflic acid or potassium nonaflate and TMSCl in boiling acetonitrile, whereas the stronger Friedel-Crafts catalyst $SnCl_4$ is effective at room temperature. Table A summarizes typical examples of one step–one pot syntheses of pyrimidine nucleosides.



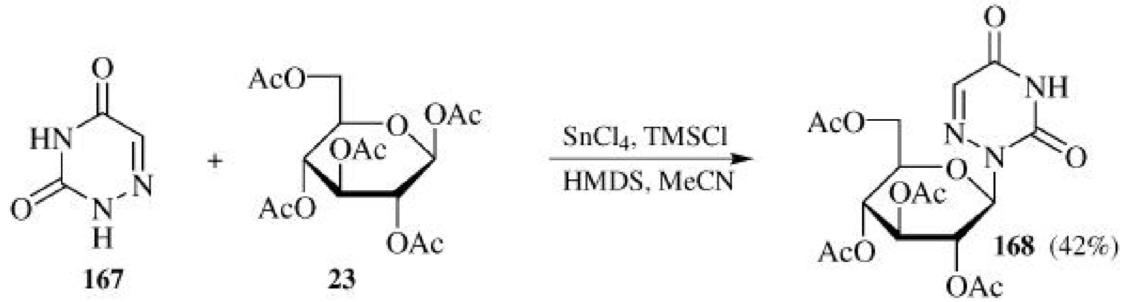
2-Thiouracil (**165b**) with $SnCl_4$ as catalyst gives 2-thiouridine-2 ,3 ,5 -tri-*O*-benzoate (**166b**) in ~ 60% yield. The more basic 5-methoxyuracil (**165c**) reacts with **18** in the presence of potassium nonaflate/TMSCl/HMDS to afford crystalline 5-methoxyuridine-2 ,3 ,5 -tri-*O*-benzoate (**166c** = **81b**) in 71% yield. The analogous reaction of N^4-acetyl cytosine (**165d**) with **18** followed by saponification with methanolic ammonia gives 56% of pure crystalline cytidine. (189)

Table A. One Step - One Pot Reactions with Sugar 18

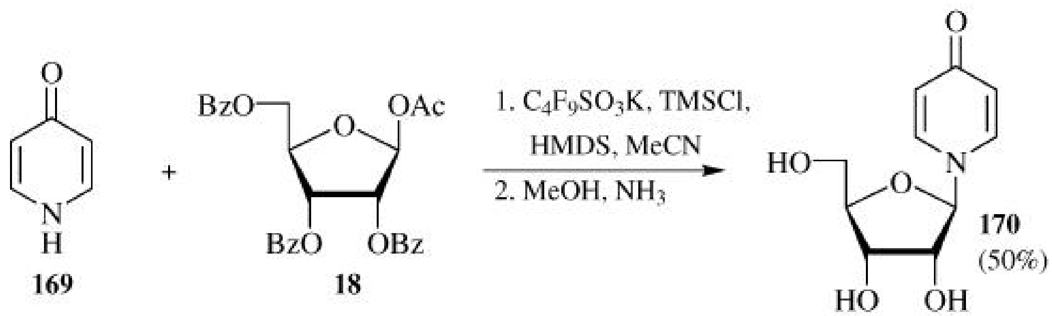
Base	Acid or Salt	TCS/HMDS	Conditions	Acylated Nucleoside
165a	CF_3CO_3H	1.2/1.1	83°, 1 h	**166a** (81%)
165a	$C_4F_9SO_3K$	3.1/0.7	83°, 14 h	**166a** (84%)
165a	$SnCl_4$	0.8/0.8	24°, 2 h	**166a** (83%)
165b	$SnCl_4$	0.8/0.8	24°, 7 h	**166b** (59%)
165c	$C_4F_9SO_3K$	3.1/0.7	83°, 20 h	**166c** (71%)
165d	$C_4F_9SO_3K$	3.1/0.7	83°, 27 h	**166d** (56%)

6-Azauracil (**167**) reacts with **23** in the presence of $SnCl_4$/TMSCl/HMDS to furnish the crystalline protected nucleoside **168** in 42% yield. The rather basic

4-pyridone (**169**) and **18** are converted by potassium nonaflate/TMSCl/HMDS followed by saponification to the free nucleoside **170** in 50% yield. (189)



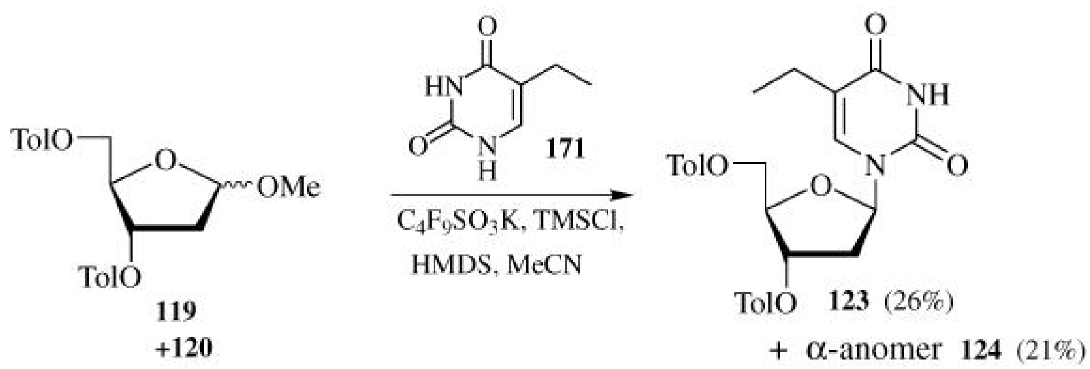
167 23 168 (42%)

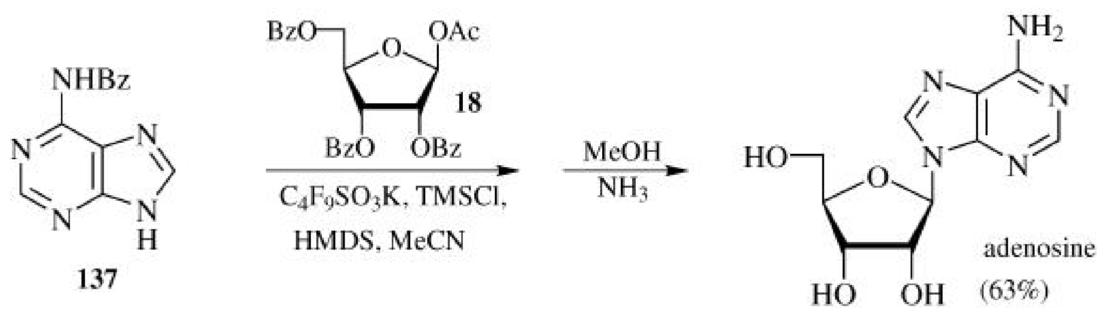


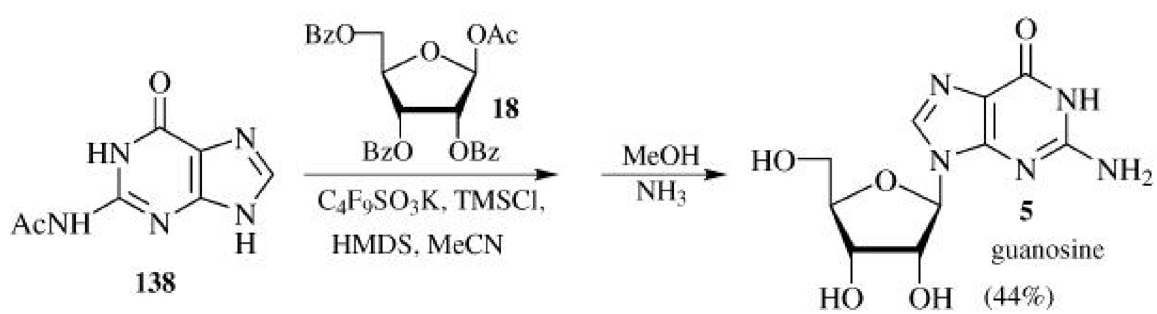
169 18 170 (50%)

The oily mixture of anomers **119** and **120** furnishes with potassium nonaflate/TMSCl/HMDS primarily the kinetically controlled 1-cation of the furanose, which reacts in situ with 5-ethyluracil (**171**) to give 26% of the β -anomer **123** and 21% of the corresponding α -anomer **124**. (189)

The purine bases *N*[6]-benzoyladenine (**137**) and *N*[2]-acetylguanine (**138**) react with **18** in the presence of potassium nonaflate/TMSCl/HMDS, affording after saponification with methanolic ammonia, crystalline adenosine in 63% and crystalline guanosine in 44% yield, respectively. (189)





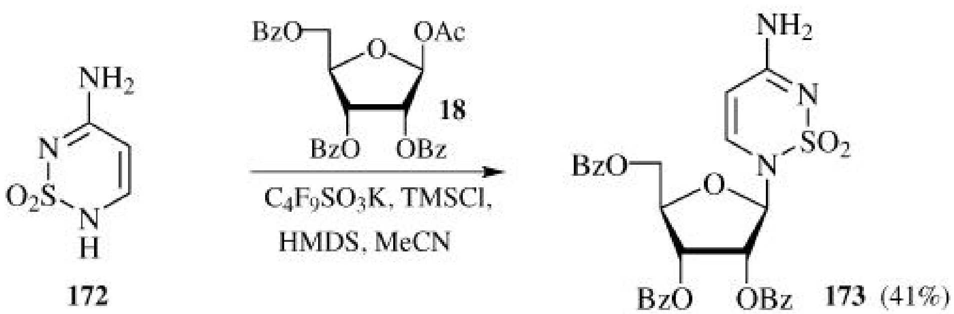


In 1,2-dichloroethane as solvent, increased salt concentrations cause increased formation of N^3-nucleosides as well as N^1,N^3-dinucleosides. Although these increased salt concentrations are usually irrelevant in acetonitrile, the reaction of 6-methyluracil with **18**, which is particularly sensitive to added salts or impurities, affords even in acetonitrile in the presence of potassium nonaflate/TMSCl/HMDS only 20–25% of 6-methyluridine-2 ,3 ,5 -tri-*O*-benzoate (**85**) besides the undesired N^3-nucleoside **86** and the N^1,N^3-bis(riboside) **87**. (189)

The one-pot reaction of 2-bromohypoxanthine with tetra-*O*-acetyl- β

-D-ribofuranose (**17**) in acetonitrile can be performed by initially heating 2-bromohypoxanthine with BSA, then adding **17** and TMSOTf to give initially more N^7- than N^9-nucleoside (HPLC). This ratio changes rapidly within 15 minutes, especially in the presence of excess **17**, to afford 75% of the N^9-nucleoside and 10% of the N^7-nucleoside. (190)

The cytosine analog **172** gives the protected cytidine analog **173** in 41% yield. (191)



Interestingly, the one-pot procedure employing $SnCl_4$ as catalyst applied to thymine or N^4-benzoyl cytosine (**165e**) and methyl-4,6-di-*O*-acyl-2,3-dideoxy-α -D-glucopyranoside furnished 60–65% of the desired protected β -nucleosides and only 18–20% of the α -nucleosides. By comparison, the corresponding reaction of N^2-isobutyrylguanine with $SnCl_4$ or TMSOTf yields complicated α / β mixtures of the corresponding N^9- and N^7-nucleosides. (192)

Equally simple is an alternative one-pot synthesis of purine nucleosides (86-86a) and cytidines. (192e) In this procedure purines such as adenines, (86b,192a–j) N^6-benzoyl (192m,n,p) or N^6-octanoyladenine (**137**), (86-192g) 6-chloropurine, (192a) 2,6-dichloropurine (**25**), (86a-192a) N^2-palmitoylguanine, (86) or N^4-acyl cytosines (180,192f,o) are reacted with 2 α -acyloxysugars such as **18** in the presence of 1–2 equivalents of $SnCl_4$ or $AlCl_3$ (86) in 1,2-dichloroethane or acetonitrile. The excess $SnCl_4$ apparently forms partially soluble σ complexes with the heterocyclic bases to afford, after the usual workup with aqueous $NaHCO_3$, the corresponding purine nucleosides (86,86a,b,192a–k) and cytidines (180,192e,f,o) in yields of up to 81%. In a recent synthesis of sinefugin, this one-step reaction failed with adenine and $SnCl_4$, whereas it succeeded with persilylated N^6-benzoyladenine in the presence of TMSOTf. (192l)

The one- or two-step methods with silylated heterocyclic bases virtually guarantee solubility of the silylated base in the reaction solvent, and thus a homogeneous, complete reaction. The free base, however, is apparently only partially soluble as its transient σ complex with $SnCl_4$, leading to incomplete reactions as well as to destruction of sugar moieties and thus lower yields. (192l)

Although the yields obtained in these one step–one pot reactions are usually somewhat lower compared to the conventional two-step procedure, the one step–one pot modification is so simple that it can also be used by investigators with limited practical experience in preparative organic chemistry.

5. Mechanism of Nucleoside Formation in the Presence of Friedel-Crafts Catalysts

5.1. Experimental Results

The weakly basic silylated 5-nitrouracil **80a** reacts rapidly with **18** and small amounts of $SnCl_4$ in 1,2-dichloroethane to form 5-nitrouridine-2′,3′,5′-tri-*O*-benzoate (**81a**) in nearly quantitative yield, (84) whereas the much more basic silylated 5-methoxyuracil (**80b**) and 5-morpholinouracil (**80c**) do not react at all with **18** in the presence of less than 1 equivalent of $SnCl_4$ (90, 193, 194) or TMSOTf. (133) Apparently, one equivalent of $SnCl_4$ (or TMSOTf) is inactivated or neutralized by σ -complex formation with the silylated bases, and only an excess of $SnCl_4$ (or TMSOTf) can lead to the formation of the electrophilic sugar cation and thus to nucleoside formation (albeit at a much lower rate than with **80a** since only small concentrations of free silylated bases **80b** and **80c** are available because of σ -complex formation). (90, 193, 194) Furthermore, besides the desired natural N^1-nucleosides **81b** and **81c**, large amounts of the undesired N^3-nucleosides **82b** and **82c** as well as the corresponding N^1,N^3-bisnucleosides **83b** and **83c** are obtained.

Replacing $SnCl_4$ by the weaker Friedel-Crafts catalysts TMSOTf or $(CH_3)_3SiOSO_2(CF_2)_3CF_3$ and switching from 1,2-dichloroethane to the more polar solvent acetonitrile, which competes with the basic silylated uracils for the Lewis acids, results in yields of up to 90% of the desired natural N^1-nucleosides **81b** and **81c**. (193, 194)

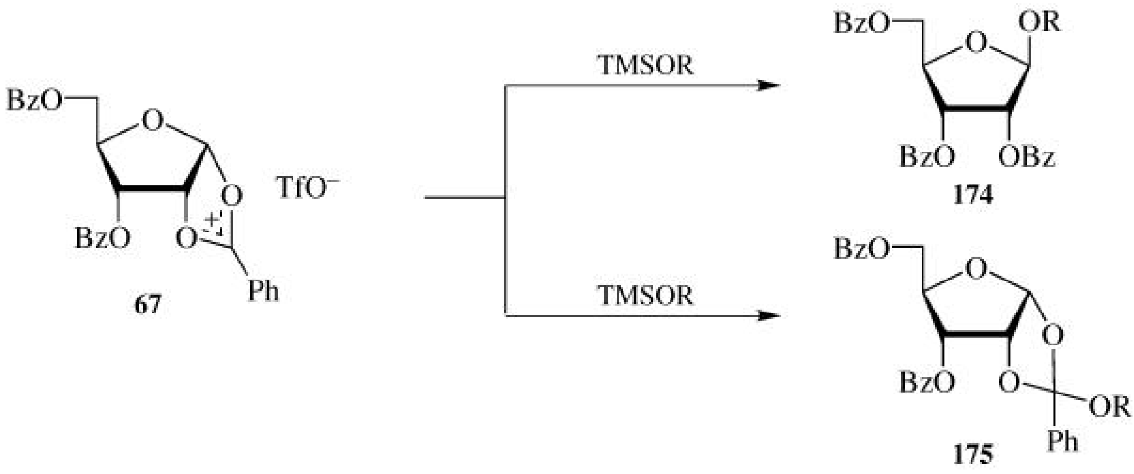
These results can be reconciled if one assumes that three reversible processes occur during nucleoside formation: (a) reaction of the peracylated sugar **18** with the different Friedel-Crafts catalysts to give the rather stable electrophilic sugar cations **35** or **67**; (b) competing reversible formation of σ complexes between the silylated bases and the different Friedel-Crafts catalysts—with sugar moieties containing basic benzyl ether groups, TMSOTf will also form weak σ complexes whereas $SnCl_4$, $TiCl_4$, or Et_2AlCl will give stronger chelate-type complexes that consume additional amounts of catalyst; and (c) reaction of the electrophilic sugar cation with the uncomplexed free silylated bases to form the nucleoside bond. (193, 194)

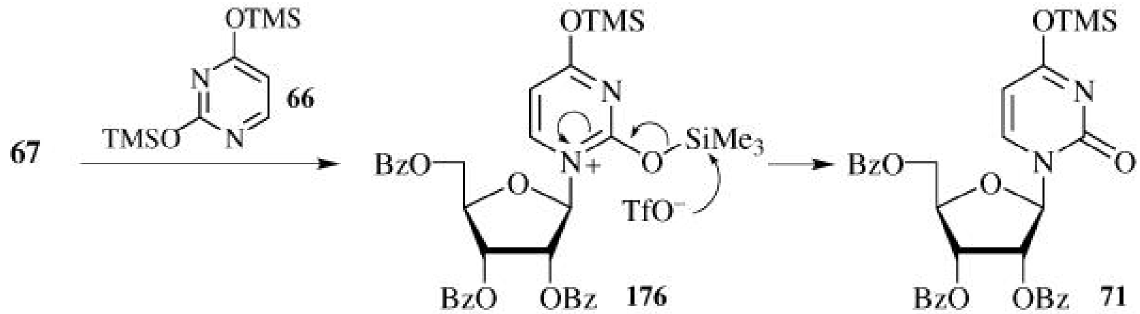
In the first process, the Friedel-Crafts catalysts $SnCl_4$, TMSOTf, $(CH_3)_3SiOSO_2(CF_2)_3CF_3$, or $TMSClO_4$ convert peracylated sugar **18** to the corresponding 1,2-acyloxonium salts **67** as the only electrophilic sugar moiety, with concomitant formation of either $SnCl_4OAc^-$ orCF_3SO_3–, $C_4F_9SO_3$– or ClO_4^- and silylated acetic acid TMSOAc. (193, 194)

These cyclic 1,2-acyloxonium salts should, however, always be generated in the presence of the nucleophilic silylated bases since all these salts derived from 1-acyloxy-, 1-alkoxy-, or 1-halofuranoses or pyranoses rearrange gradually in the presence of Lewis acids such as $SbCl_5$ or $BF_3 \cdot OEt_2$ in acetonitrile or nitromethane to isomeric cyclic 1,2-acyloxonium salts (195–198a) and might furthermore react with acetonitrile in a Ritter reaction (199-204) to give protected 1-acetylaminosugar derivatives.

Under these reversible and thus thermodynamically controlled conditions, the nucleophilic silylated bases can only attack the furanose (or pyranose) sugar cation **67** or **115** from the top (the β side) to afford the β -nucleosides with only minute amounts of the corresponding α -nucleosides as postulated by the Baker rule. The latter states that a base should approach the sugar ring from the side opposite the group at position 2, regardless of the relative configuration of $C_1 – C_2$. (205) Peracylated 1-*O*-acyl- and in particular 1-*O*-acetyl-peracetylated di- and oligosaccharides (98) afford analogously the corresponding 1,2-cyclic acyloxonium salts with $SnCl_4$ or TMSOTf, which are converted by silylated bases to the corresponding acylated nucleosides.

Other nucleophiles such as alcohols or silylated alcohols react analogously under these reversible conditions with cyclic acyloxonium triflates **67** to give the corresponding β -glycosides **174** in often excellent yields, (206) which are thermodynamically favored compared to the orthoesters **175**. (210, 211) Although this new methodology has found wide application, (207) only rarely is the origin of sugar cations such as **67** discussed. (208–209d)

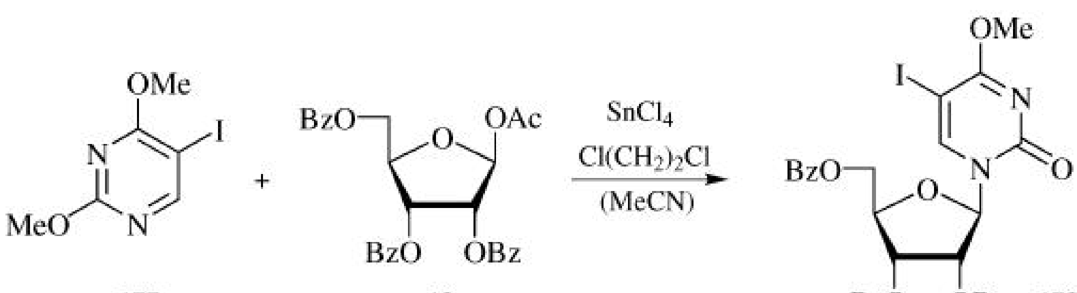




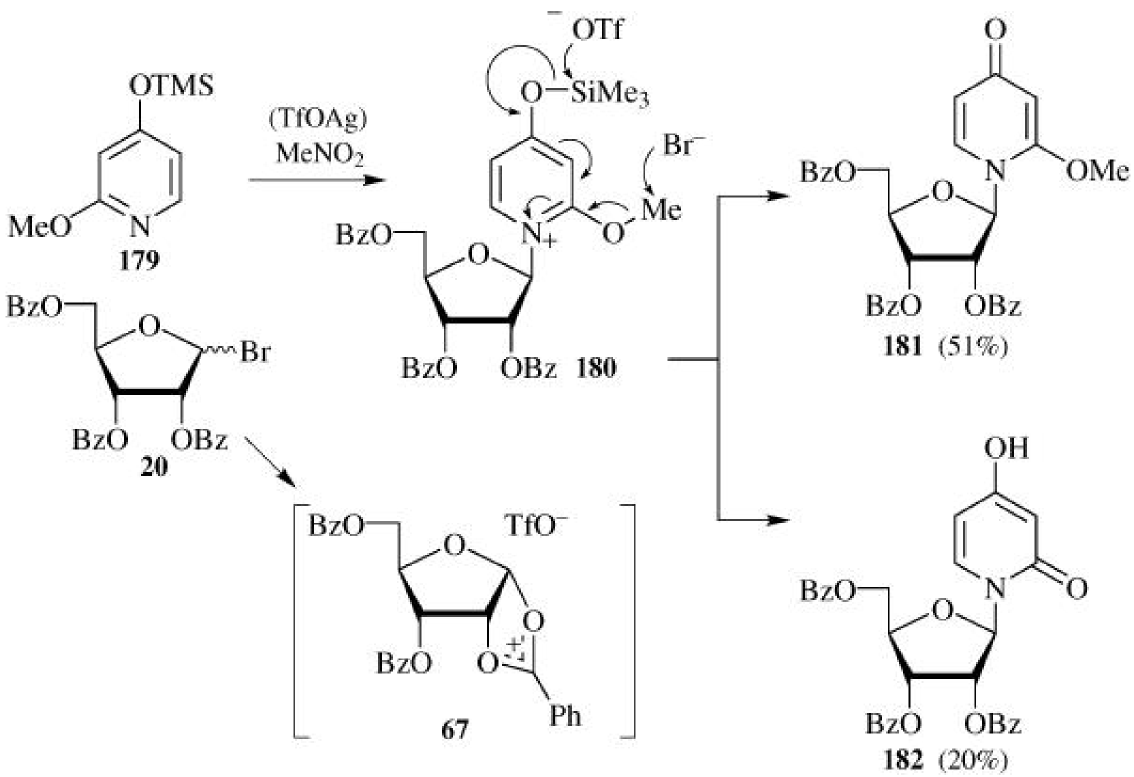
After β attack of silylated uracil **66** on sugar cation **67**, the α -trimethylsilyloxy group in the intermediate salt **176** reacts with the triflate anion to regenerate TMSOTf (or with $SnCl_4OAc^-$ to form trimethylsilyl acetate as well as regenerated $SnCl_4$), thus forming protected uridine **71**.

The classical 2,4-dialkoxypyrimidines such as 5-iodo-2,4-dimethoxypyrimidine (**177**) react analogously with sugar **18** in the presence of $SnCl_4$ with cleavage of the α -alkoxy group to give the corresponding 4-alkoxynucleosides **178**, (84) whereas with heterocyclic bases such as 4-trimethylsilyloxypyridine (**92a**) the 4-trimethylsilyloxy group reacts smoothly with triflate anion (or $SnCl_4OAc^-$) to give the protected nucleoside **93a**. (133)

On reaction of 2-methoxy-4-trimethylsilyloxypyridine (**179**) with **20** and silver triflate in nitromethane, the intermediate pyridinium triflate **180** is cleaved by attack of the hard triflate anion on the hard 4-trimethylsilyloxy group to furnish the protected 2-methoxy-4-pyridone nucleoside **181** in 51% yield. Reaction of **179** with **20** in the absence of silver triflate leads to the pyridinium bromide intermediate **180**, in which the soft 2-methoxy group is cleaved by the soft bromide ion to give, after hydrolysis of the 4-trimethylsilyloxy group, nucleoside **182** in 20% yield. (212-212a)

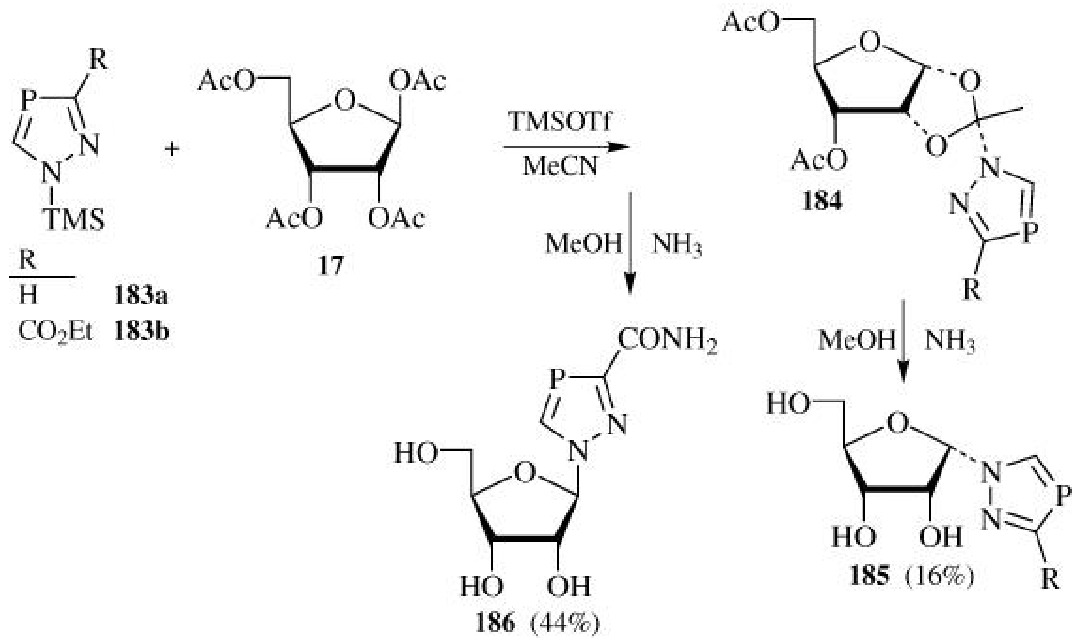


177 18 178



As emphasized above, under reversible and thus thermodynamically controlled conditions, β -nucleosides are normally obtained nearly exclusively. The only exceptions to this near exclusive β attack on **67** (with TfO^{-}, $SnCl_4OAc^{-}$, or $C_4F_9SO_3^{-}$ as counterions) can apparently occur when:

a. the heterocyclic base contains strongly polarized or negatively charged groups, which can associate with the positively charged α side of the sugar cation in **67**. This has been demonstrated in silylated 2-nitroimidazole (213-213a) or silylated 1,2,4- λ^3-diazaphosphole (**183a**), which is converted by TMSOTf to the α-anomer **185** in 16% yield via the orthoester intermediate **184**. The structure of **185** was confirmed by single crystal X-ray analysis. (214) Not unexpectedly, the analogous reaction of **183b**, which contains an electron-withdrawing ester group that impedes the formation of **184b**, furnishes the crystalline β -nucleoside **186** in 44% yield after saponification by methanolic ammonia; (214)

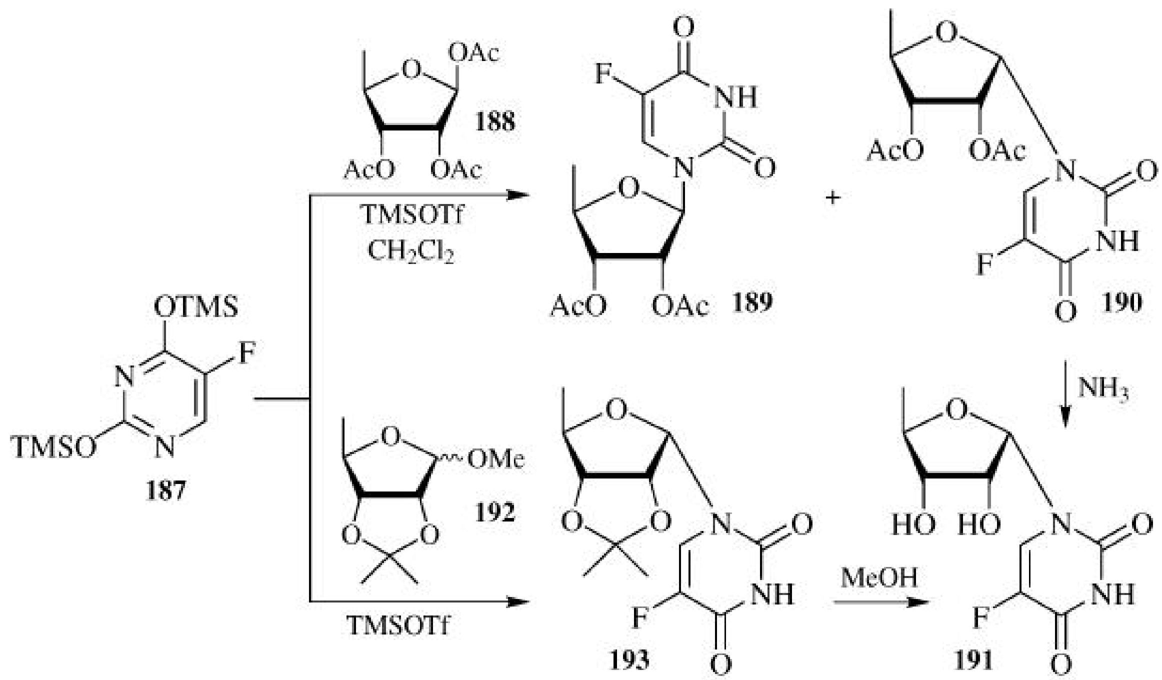


b. the sugar cation is apparently not formed quantitatively as in the case of the 4-thiosugars; (215) or

c. when the sugar 1,2-acyloxonium salt contains polar groups such as amide or nitro on the α side. (216, 217) Peracylated glucosamides, however, in which the basic nitrogen moiety is protected or neutralized by a strongly electron-attracting *N*-trifluoroacetamido- or *N*-2,4-dinitrophenyl group give more than 80% of the β -nucleoside with persilylated uracil and $SnCl_4$; (218) or

d. a stabilized cation can form above the plane of the sugar (e.g., as a chloronium cation in 1-*O*-acetyl-3,4-*O*-benzoyl-2-chloro-2-deoxy- α -D-arabinose), resulting exclusively in α -nucleoside formation. (219)

Two publications (220, 221) report the isolation of ~ 5% α -nucleoside **190** in addition to the expected β -nucleoside **189** during the reaction of silylated 5-fluorouracil (**187**) with 5-deoxy-1,2,3-tri-*O*-acetyl- β -d-ribofuranose (**188**) in the presence of TMSOTf in CH_2Cl_2. The β -nucleoside **189** rearranges on standing for 1 week with TMSOTf in CH_2Cl_2 to form 2% of the α -nucleoside **190**. The assignment of the structure of the α anomer **190** is based on the identity of the free nucleoside **191** with the α -nucleoside obtained by reaction of **187** with 1-*O*-methyl-2,3-isopropylidene-5-deoxy-D-ribofuranose (**192**) in the presence of TMSOTf to give **193** and **191** on subsequent acid hydrolysis of the isopropylidene group. (221)The analogous reaction of silylated thymine with 2,3-*O*-isopropylidene-1,5-di-*O*-*p*-toluoyl- β -D-ribofuranose gives 65% of the protected α -nucleoside in the presence of TMSOTf. (222, 223)

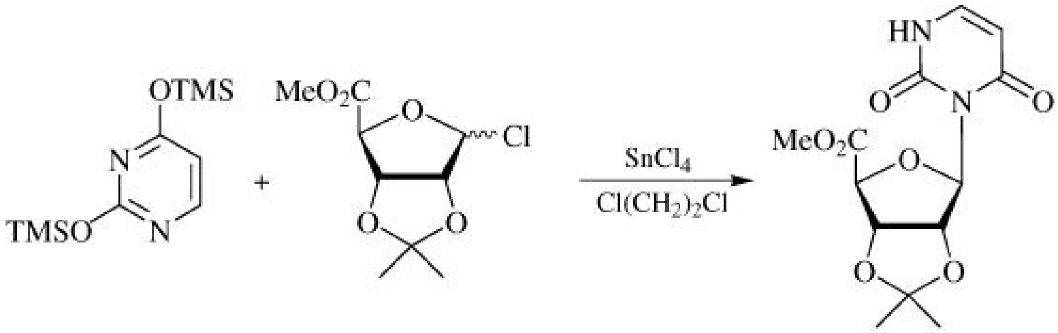


In the synthesis of nucleosides with 4-thiosugars, 2- α -benzoyloxy- or 2- α -(4-methoxy)benzoyloxy groups stabilize the cyclic cations (such as **67**) much better than a 2- α -acetoxy moiety to give more or exclusive formation of β -nucleosides.

More extensive application of HPLC to mother liquors of the desired β-nucleosides will reveal more cases where protected or free α -nucleosides can be detected in small amounts. During the synthesis of pteridine-ribofuranosides, the formation of small amounts of the corresponding α -nucleosides was observed. (223a)

The related reaction of silylated uracil **66** with 1-chloro-2,3-*O*-isopropylideneuronic acid methyl ester (**194**) in the presence of $SnCl_4$ furnishes the β -N^3-nucleoside **195** in 32% yield. (224) TMSOTf and $SnCl_4$ behave differently in the presence of polar groups such as ester and amide functionalities, since $SnCl_4$ binds more strongly to the carbonyl group and might conceivably bind more tightly than TMSOTf to the α -2,3-isopropylidene moiety in **194**, thus blocking the αside to result in formation of the β -N^3-nucleoside **195**.

Whereas the 2,3-*O*-isopropylidene group such as in **192** can only stabilize the 1-cation in the presence of chelate-forming $SnCl_4$, 2- α -methoxy, (225,226,226b,c) 2- α -silyloxy, (226-226a) 2- α -phenylsulfenyl, (227–229,229a) 2- α -phenylselenyl, (230, 231) 2- α -



66 194 195 (32%)

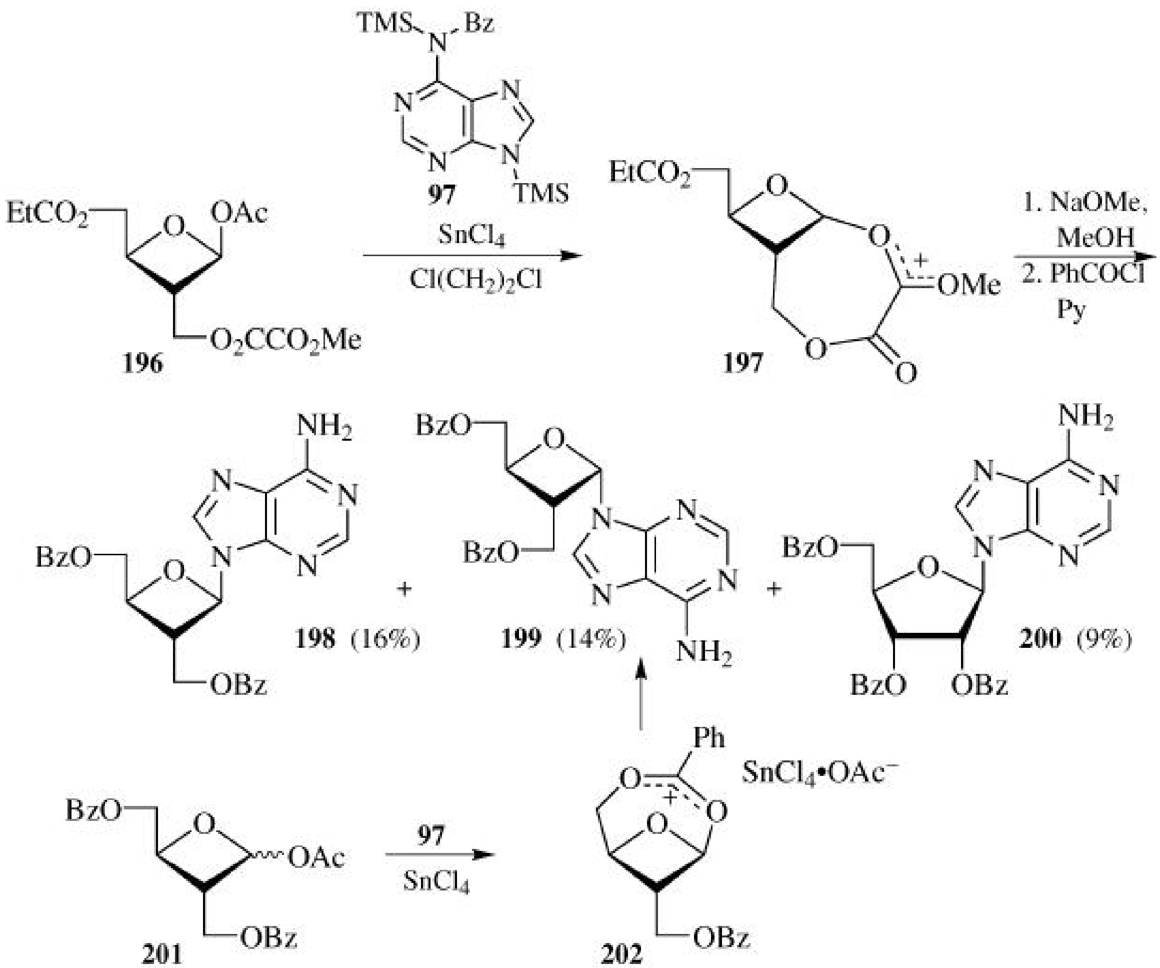
tosyloxy, (192k) as well as 2,3-epimino groups (232) stabilize the 1-cation from the α side with $SnCl_4$ as well as with TMSOTf, resulting in the predominant formation of β -nucleosides. It should be realized, however, that reactions of **22** containing a 2- β -benzyloxy group give predominantly β -nucleosides with silylated bases in the presence of $SnCl_4$. (84)

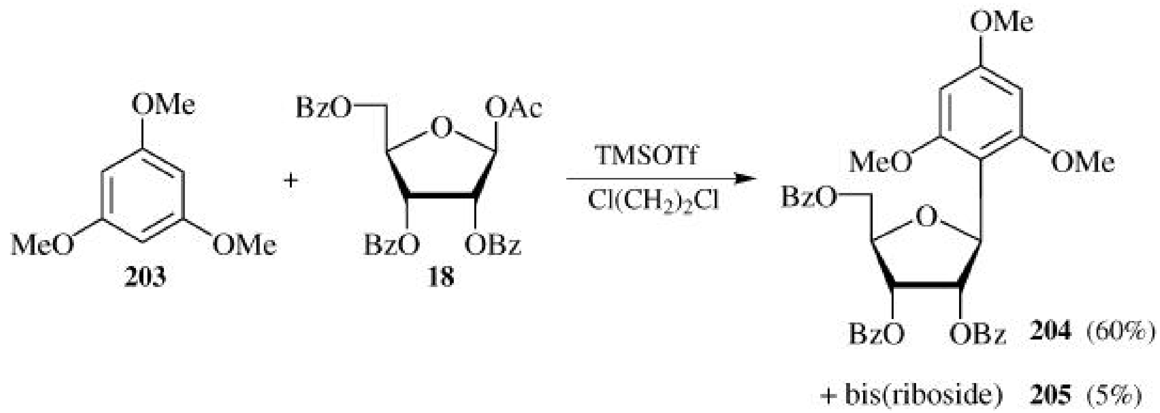
In the synthesis of oxetanocin, the sugar derivative **196** with a stabilizing oxalyloxy group reacts with silylated *N*-benzoyladenine (**97**) in the presence of $SnCl_4$ to give via the bridged cation **197** (containing a less strained and therefore more stable bicyclo[5.2.0] system) after hydrolysis and *O*-benzoylation 16% of di-*O*-benzoyloxetanocin (**198**), 14% of the corresponding α -nucleoside **199**, as well as 9% of di-*O*-benzoylepioxetanocin (**200**). (233) The corresponding di-*O*-benzoylsugar **201** affords the cation **202** with **97** in the presence of $SnCl_4$ and thus exclusively the α -nucleoside **199**. (233)

Since the rather stable 1,2-acyloxonium ions **67** (from **18** and TMSOTf) are only weak electrophiles, they react only with electron-rich nucleophilic aromatic systems such as 1,3,5-trimethoxybenzene (**203**) to give 60% of the *C*-nucleoside **204** and 5% of the corresponding bis(nucleoside) **205**. (133) This reaction was later applied in a slightly modified form. (133a–c) Although *C*-nucleosides (39-44) are not the subject of this review, these results demonstrate the close relationship between the Friedel-Crafts catalyzed Silyl-Hilbert-Johnson reaction and the classical Friedel-Crafts reaction.

5.2. Reversible s -Complex Formation between Silylated Bases and Friedel-Crafts Catalysts

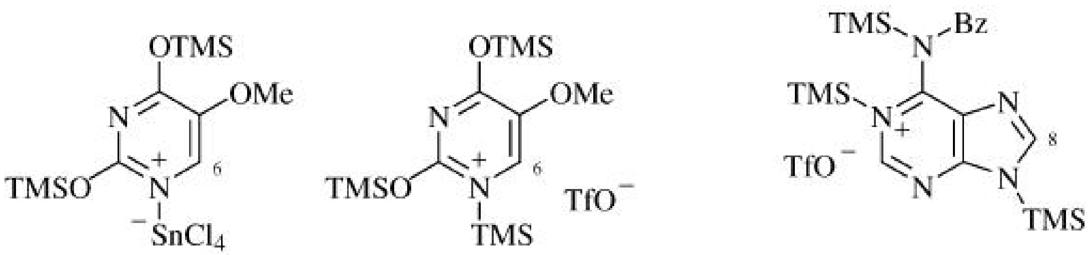
The formation of σ complexes between Friedel-Crafts catalysts and silylated bases is dependent on the acidity of the Friedel-Crafts catalysts as well as on the basicity of the silylated heterocyclic bases. Although the pK_a values for silylated heterocyclic bases have not been determined, the pK_a values of the closely related methoxypyrimidines and pyridines (234) can be used for comparison purposes: the increase in basicity from 2-methoxypyridine (pK_a 3.2) to 4-methoxypyridine (pK_a 6.5) is striking and explains why 4-trimethylsilyloxypyridine (**92a**) forms such strong σ complexes and why **92a** is converted to the corresponding nucleoside **93a** only under forcing conditions. (99, 133) The basicity of 2,4-dimethoxypyrimidine (pK_a 3.1) is increased to pK_a 3.63 on introduction of an electron-releasing





5-methyl group. Since the basicities of amino heterocycles such as cytosine and in particular adenine or guanine are decreased on acylation to the N^4-benzoyl or N^4-acetyl cytosines, N^6-benzoyladenine or N^2-acetyl- or N^2-isobutyrylguanine, it is obvious that these *N*-acylated bases and their analogs are commonly employed in their silylated form for Friedel-Crafts catalyzed nucleoside synthesis in preference to the more basic silylated amino heterocycles, resulting in faster and cleaner nucleoside formation. With the more basic silylated cytosine **222**, at least two equivalents of $SnCl_4$ had to be employed to effect a smooth preparation of **224**, (235) whereas other nucleoside forming reactions employing sensitive protected 2-deoxy sugars and silylated cytosine in the presence of *tert*-butyldimethylsilyl triflate failed. (236)

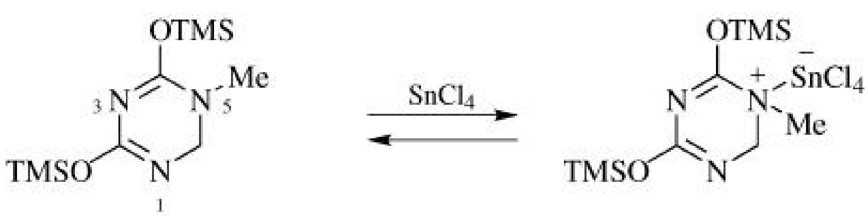
The structures of the σ complexes between silylated 2-pyridone and silylated 5-methoxyuracil and $SnCl_4$ as well as TMSOTf can be derived from their ^{13}C NMR spectra. (194) The resulting upfield shifts of the C^6-carbon atom adjacent to the quaternized nitrogen atoms in the pyridine and pyrimidine series give good information on the σ complexes between the silylated bases and the particular Lewis acids. Tin tetrachloride, as the stronger Lewis acid, binds more tightly to the N^1-nitrogen of silylated 5-methoxyuracil to give **206** than does TMSOTf to give **207**. Whereas one equivalent of $SnCl_4$ leads to practically quantitative formation of the σ complex **206**, nearly five equivalents of TMSOTf are needed to effect quantitative formation of the related σ complex **207**. (193, 194)



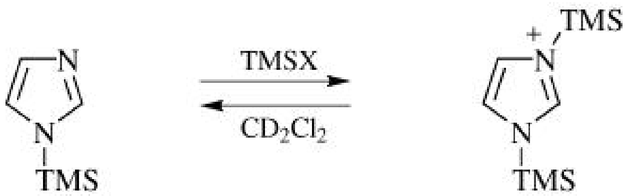
206 **207** **208**

The pronounced upfield shift of the C^8-carbon atom in the ^{13}C NMR spectrum of silylated N^6-benzoyladenine (**97**) on addition of increasing amounts of TMSOTf can be interpreted by σ -complex formation at the N^1-nitrogen, the center of highest electron density as depicted in **208**. (194) These conclusions are in agreement with the ^{13}C NMR spectra of protonated adenine in solution. (237)

The interaction between the disilylated 5-methyl-5,6-dihydro-*sym*-triazine-2,4(1*H*,3*H*)dione (**209**), containing a basic tertiary nitrogen atom, and $SnCl_4$ leads apparently to a σ complex between this basic tertiary nitrogen atom and $SnCl_4$ to form **210**, in which the basicity of the N^3-nitrogen is decreased. Since the N^3-nitrogen in **210** is sterically more encumbered than the N^1-nitrogen, exclusive formation of the desired N^1-nucleoside is observed. (238, 239) Thus the basic N^5-nitrogen group does not interfere with nucleoside synthesis. Likewise a free 5-methylaminomethyl group in silylated 2-thiouracil readily gives the anticipated protected nucleoside in the presence of excess catalyst. (126)



209 **210**

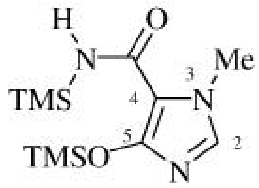


211 **212** X = ClO_4^-, I^-, TfO

Following the reaction of silylated imidazole **211** and TMSX (X = ClO_4^-, I^-, TfO^-) in CD_2Cl_2 by ^{29}Si-NMR measurements demonstrates that in the equilibrium between **211** and its σ complexes **212** the formation of **212** is most favored for X = ClO_4^- > I^- > TfO^-. (240) Thus $(CH_3)_3SiI$ apparently has a stronger tendency to form σ complexes with **211** than TMSOTf. No quantitative data, however, nor any discussion of earlier work (194) on such σ complexes are provided. (240)

During studies on the synthesis of bredinin, (241-243) the structure of persilylated imidazole **214** was established by MS and ^{13}C NMR and comparison with *N*-methylimidazole **213**. Imidazole **214** was then treated with increasing amounts of TMSOTf; the ^{13}C NMR spectra of the resulting σ complex **214** **215** or **216** showed the expected upfield shift of the C-5 signal. The maximum shift, however, was not reached even on addition of 1.4 equivalents of TMSOTf. (242)

Addition of equivalent amounts of the stronger Lewis acid $SnCl_4$ to **214** leads to the fully complexed compound **217**, in which the C-5 signal is only slightly shifted downfield. In contrast, the carboxamide carbon undergoes a pronounced downfield shift, whereas the adjacent C-4 carbon is shifted upfield. These data support the structure of **217** as a σ complex between the silylated carboxamide group and $SnCl_4$. (242) Such σ complexes of carbonyl groups with $SnCl_4$ or $TiCl_4$ have recently been investigated and reviewed. (244-246) Complexes of Lewis acids such as $TiCl_4$ with peracylated sugars have also been described (247, 248) and should be taken into account when reacting complex sugars such as peracylated disaccharides (98) or **515** (see p. 99). (160)



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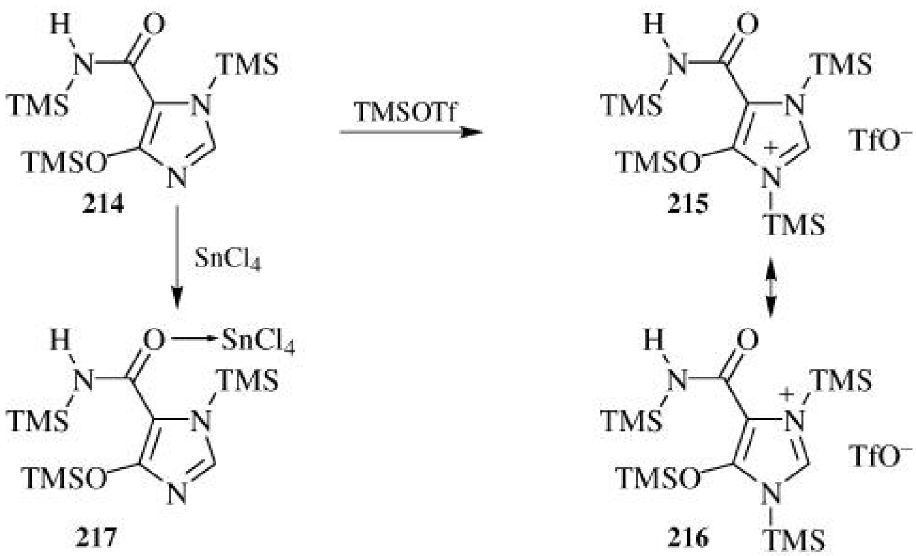
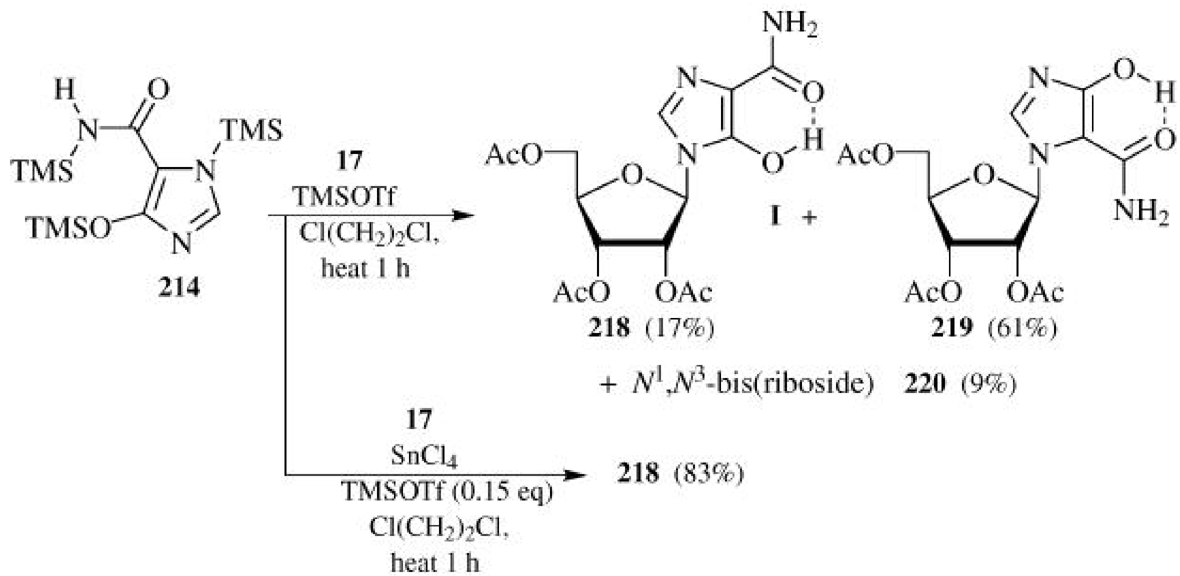
As a consequence of these different σ complexes between **214** and TMSOTf to give **215** **216** and of **214** with $SnCl_4$ to yield **217**, the reaction of **214** with **17** in the presence of TMSOTf leads to only 17% of the desired protected bredinin **218** and 61% of the undesired N^3-nucleoside **219** as well as 9% of the N^1,N^3-bis(riboside) **220**. On the other hand, use of 1 equivalent of $SnCl_4$ (to form **217**) followed by additional catalytic amounts of TMSOTf to generate the reactive sugar



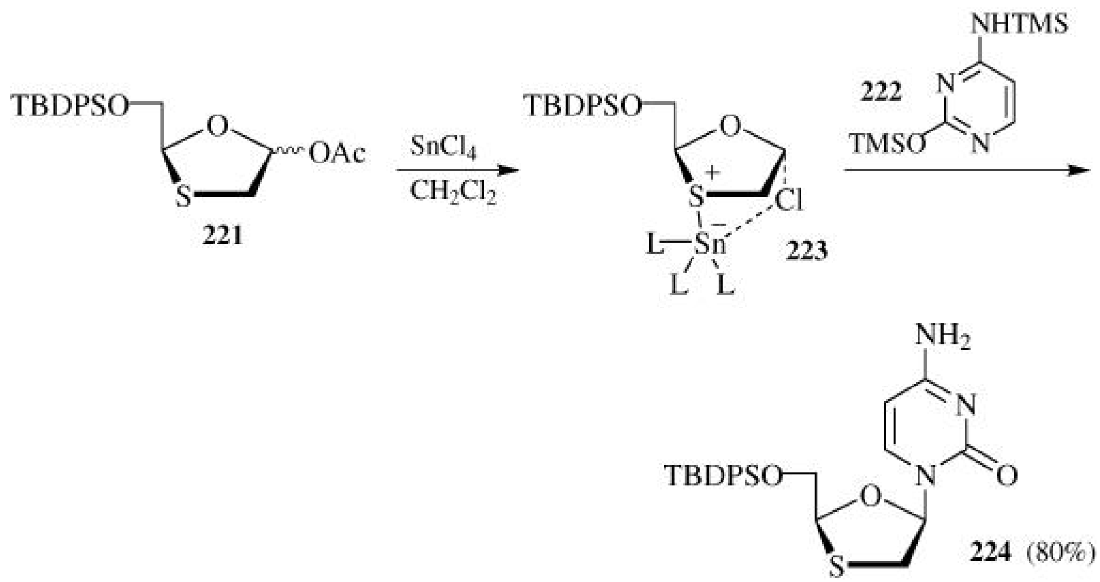
cation affords protected bredinin **218** in 83% yield. (242) It seems probable that the additional catalytic amount of TMSOTf can be replaced by a catalytic amount of $SnCl_4$.

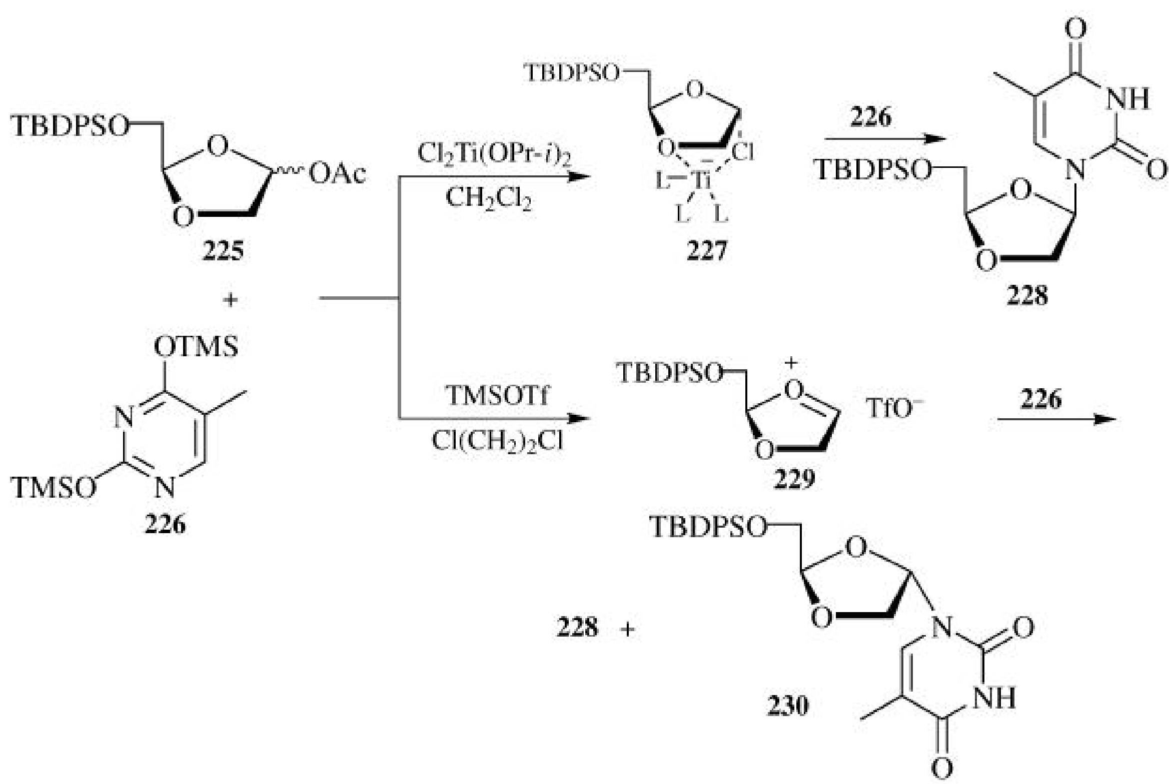
There are thus differences in catalytic behavior between $SnCl_4$ and TMSOTf if polar groups such as amides or esters are present in the silylated heterocyclic base or in the sugar. Note also the different reactions of persilylated N^2-acetylguanine (**108b**) with **18** in the presence of $SnCl_4$ and TMSOTf in dichloroethane. (142)



In a striking example of σ complexes of the sugar moiety with a Lewis acid, thiosugar **221** reacts with silylated cytosine (**222**) in the presence of 2 equivalents of $SnCl_4$ to form (via σ complex **223**) exclusively β anomer **224** in 80% yield, whereas with TMSOTf as catalyst a 1:1 β / α -mixture is produced. (235) In the case of the oxasugar **225**, dichlorotitanium diisopropoxide leads via **227** to exclusive formation of the β -nucleoside **228**, whereas TMSOTf gives again a 1:1 β / α -mixture. (235) Other studies, however, have demonstrated that during or prior to the formation of **223** or **227** a cation is also formed with $SnCl_4$ at the cyclic acetal or thioacetal carbon leading to completely racemized nucleosides. (249) In contrast to $SnCl_4$ or dichlorotitanium diisopropoxide as catalysts, TMSOTf converts the sugar derivative **225** into cation **229**, which reacts with silylated thymine **226** to give a 2:1 mixture of the optically active β -nucleoside **228** and the α anomer **230**. Thus reactive groups in the silylated base as well as in the sugar moiety have to be considered in choosing the optimal Lewis acid catalyst.

For additional publications on 3- or 2-oxa-, thia-, or selenanucleosides, see Refs. 249a–k.



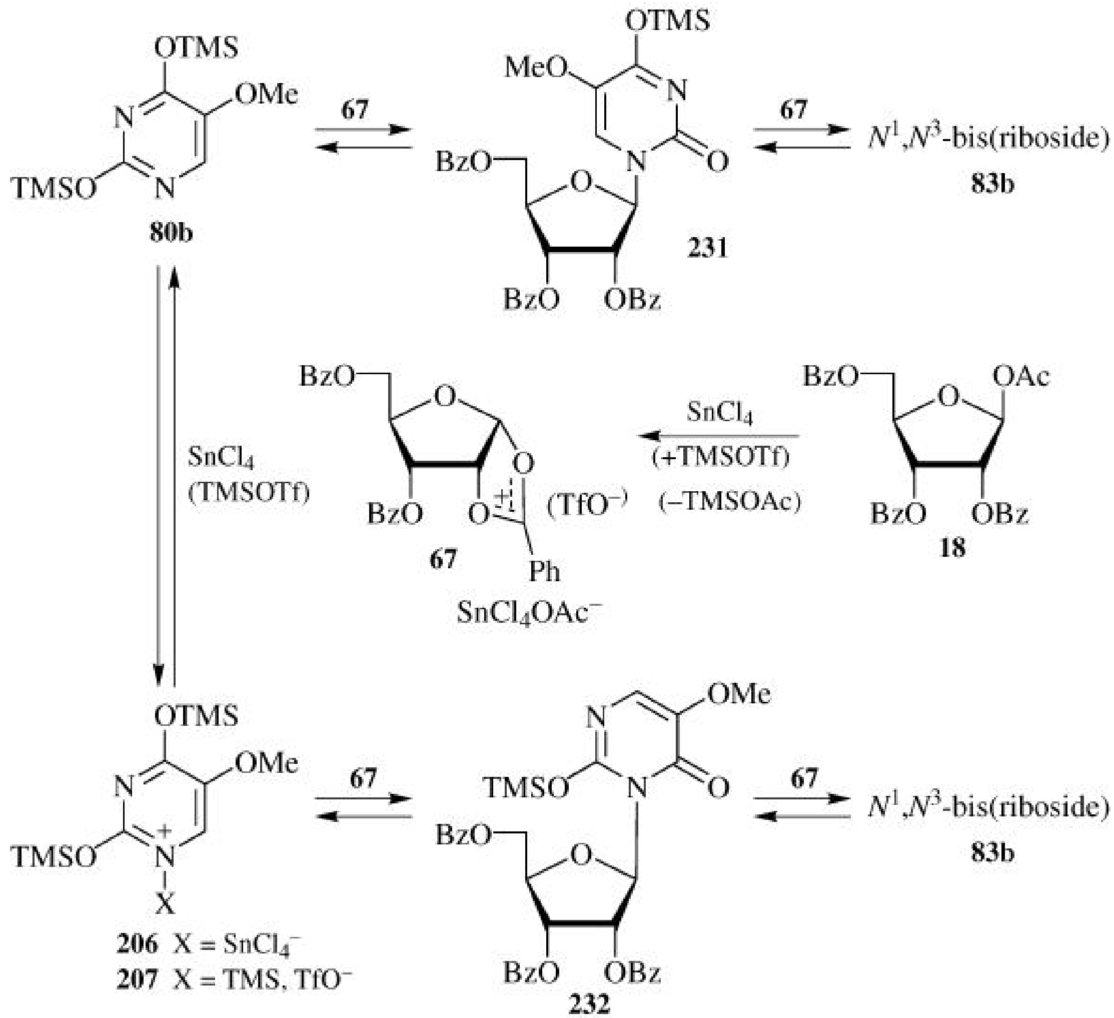


5.3. Mechanism of Pyrimidine and Purine Nucleoside Synthesis

Taking all the above results into account, the mechanism of the Friedel-Crafts catalyzed Silyl-Hilbert-Johnson synthesis of pyrimidine nucleosides is straight-forward as exemplified for the reaction of silylated 5-methoxyuracil

80b in the presence of $SnCl_4$ and TMSOTf. The reaction of **80b**, **18**, and the stronger Lewis acid $SnCl_4$ sets up an equilibrium in which the σ complex **206** between the N^1 of **80b** (the center of highest electron density) predominates in nonpolar solvents such as 1,2-dichloroethane. Since only the free silylated base **80b** will react with the electrophilic sugar cation **67** (with $SnCl_4OAc^-$ as the counterion) to form the 4-*O*-trimethylsilylated *O*-benzoylated 5-methoxyuridine **231**, and the concentration of free silylated base **80b** is rather low in the equilibrium with $SnCl_4$, nucleoside formation will be rather slow.

Furthermore, in the equilibrium between σ complex **206**, silylated base **80b** and $SnCl_4$, the $SnCl_4$ will stay close to the electron-rich center at the N^1-nitrogen. It is this slightly dissociated form, in which the N^1-nitrogen is still blocked and the N^3-nitrogen is available, that reacts with **67** to form the undesired silylated *O*-protected N^3-nucleoside **232**. Both the silylated protected N^1-nucleoside **231** as well as the corresponding N^3-nucleoside **232** can react further with **67** (with $SnCl_4OAc^-$ as counterion) to give the protected N^1,N^3-bis(nucleoside) **83b**.



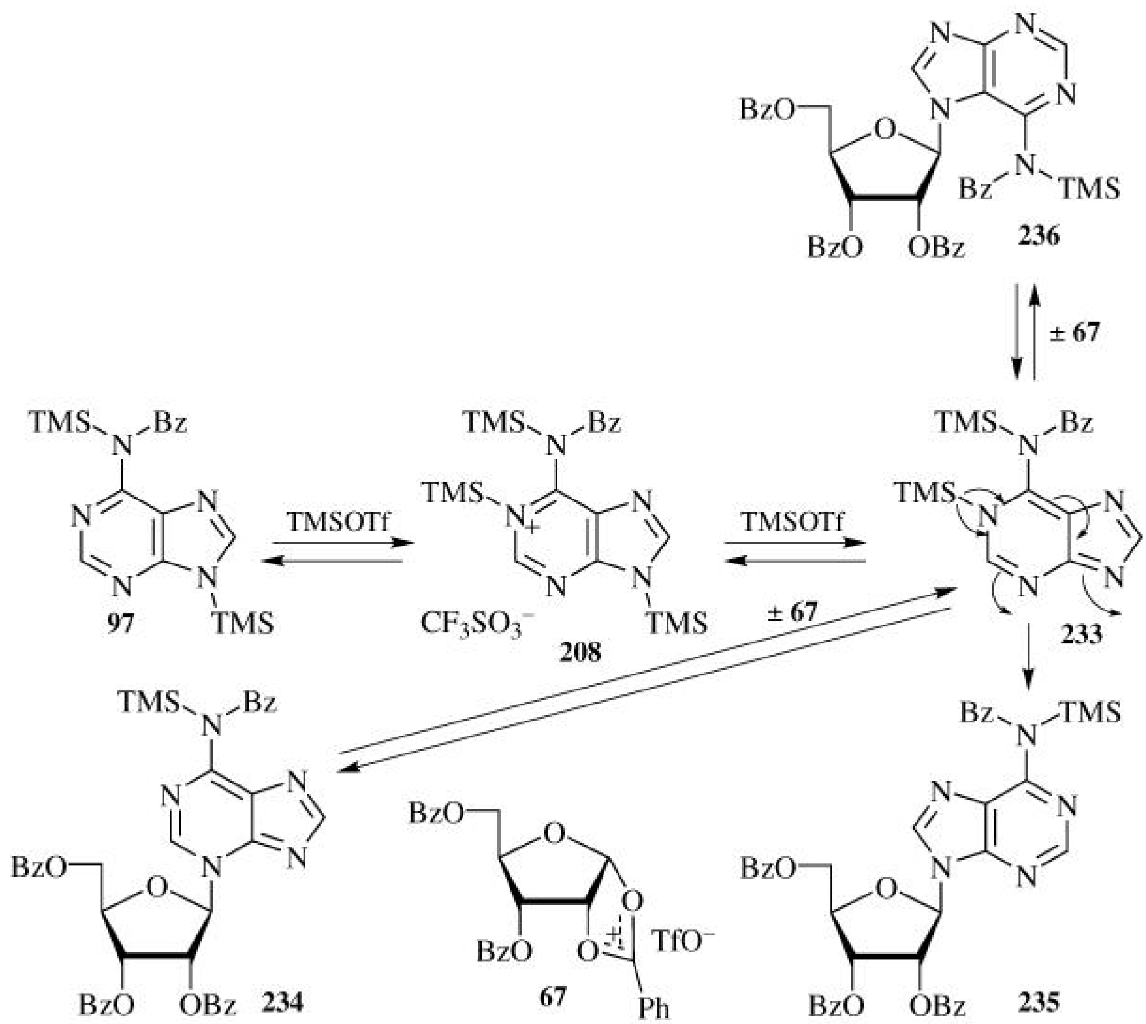
As already emphasized, the ratio of free **80b** and complexed form **206** is also dependent on the polarity of the solvent. The more nucleophilic solvent acetonitrile, which forms σ complexes with $TiCl_4$, (250) $SnCl_4$, (251) and BH_3, (252) competes with the silylated base for the electrophile and simultaneously favors the formation of the polar sugar cation **67**. Consequently, in acetonitrile there is more silylated base **80b** and more sugar cation **67** present, and thus more of the desired natural N^1-nucleoside **231** is formed.

The corresponding reaction with TMSOTf is analogous: since it is a weaker Lewis acid than $SnCl_4$, however, less σ complex **207** is formed in the equilibrium. Therefore, more free base **80b** is present and consequently more silylated N^1-nucleoside is obtained. Again, both the protected silylated N^1-nucleoside **231** as well as the protected silylated N^3-nucleoside **232** can react further with **67** to form the N^1,N^3-bis(nucleoside) **83b**. Experimental support for these equilibria is provided by the rearrangement of protected silylated N^3-nucleosides (**104**   **85**) (133) as well as by the different transglycosylations catalyzed by TMSOTf (see section on transglycosylations).

With respect to the reaction of silylated purines with peracylated sugars in the presence of TMSOTf (or $SnCl_4$) the aforediscussed σ complex between persilylated N^6-benzoyladenine **97** and TMSOTf yields the σ complex **208** as determined by ^{13}C NMR. (194) If **208** is assumed to be in equilibrium with the N^1-silyl compound **233**, then it should react readily with **67** to give the N^3-nucleoside **234** as a kinetically controlled intermediate, which can be isolated after a short reaction time (133) or rearranged in situ (**111**   **112**) to the thermodynamically most stable silylated natural N^9-nucleoside **235**. (133) Alternatively, **233** (or the isomeric **506**) could also react directly with **67** (compare the arrows in **233**) to the natural N^9-nucleoside **235** as well as to the N^7-nucleoside **236**, which would subsequently rearrange to the desired N^9-nucleoside **235**. If the reaction of **97** with **67** is followed by TLC, a number of intermediates can be discerned, which disappear during the course of the reaction. (133) Since the protected N^6-nitrogen in the N^7-nucleoside **236** interferes sterically with the sugar moiety, formation of **236** is disfavored, resulting in high yields of the protected natural adenosine **235**.

Because of the initial formation of the intermediates such as the N^3-nucleoside **234**, the formation of σ complexes between these intermediates with Lewis acids such as TMSOTf or $SnCl_4$ is necessary to induce the rearrangement of these intermediates to the thermodynamically favored protected adenosine **235** (or the corresponding protected N^9-guanosine). Consequently a less polar solvent such as 1,2-dichloroethane or toluene is advantageous for the synthesis of purine nucleosides. In contrast, the more polar acetonitrile competes with silylated purine bases for the Friedel-Crafts catalysts and impedes these rearrangements, leading to longer reaction times, some cleavage of the nucleosides, and destruction of the sugars.

In guanosine synthesis, however, the 6-trimethylsilyloxy group is less of a steric impediment so that formation of small amounts of N^7-guanosine (**110b**) is always observed in the equilibrium (cf. **108b** → **109b** + **110b** as well **113**   **114**). Consequently, introduction of a more bulky 6-triethylsilyloxy or 6-triisopropylsilyloxy group into N^2-acetylguanine might lead to formation of less N^7-guanosine.



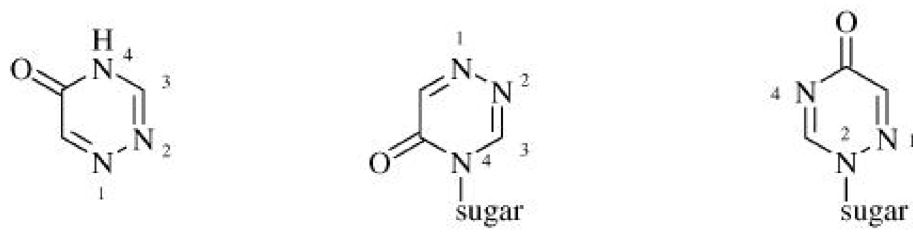
For similar investigations compare the aforediscussed synthesis of *sym*-1,3,5-triazine nucleosides (**209** → **210**) as well as imidazole nucleosides (**214** **220**).

5.4. Regioselectivity of Nucleoside Formation

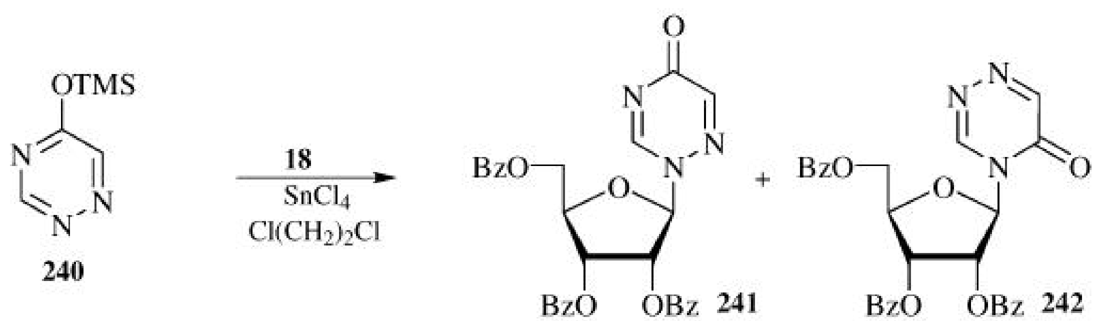
When free or silylated organic bases contain more than one nitrogen atom, each of these nitrogen atoms can in principle become attached to a sugar derivative. The formation of the resulting different nucleosides is either kinetically or thermodynamically controlled.

Whereas the regioselectivity in the synthesis of pyrimidine nucleosides (e.g., formation of the undesired *O*-nucleosides and the N^3-nucleosides) has been discussed, consideration of some principles and of additional techniques such as blocking of nitrogen functions are in order. With heterocyclic bases containing a carbonyl or thiocarbonyl group, the nitrogen atom either α or γ to the carbonyl or thiocarbonyl group is preferred for nucleoside formation. Thus in 1,2,4-triazin-5-one (**237**) only the N^2-or N^4-nitrogen can serve as a nucleophile to give either **238** or **239**. (99) Thus silylated 1,2,4-triazin-5-one **240** affords **241** as well as **242**.

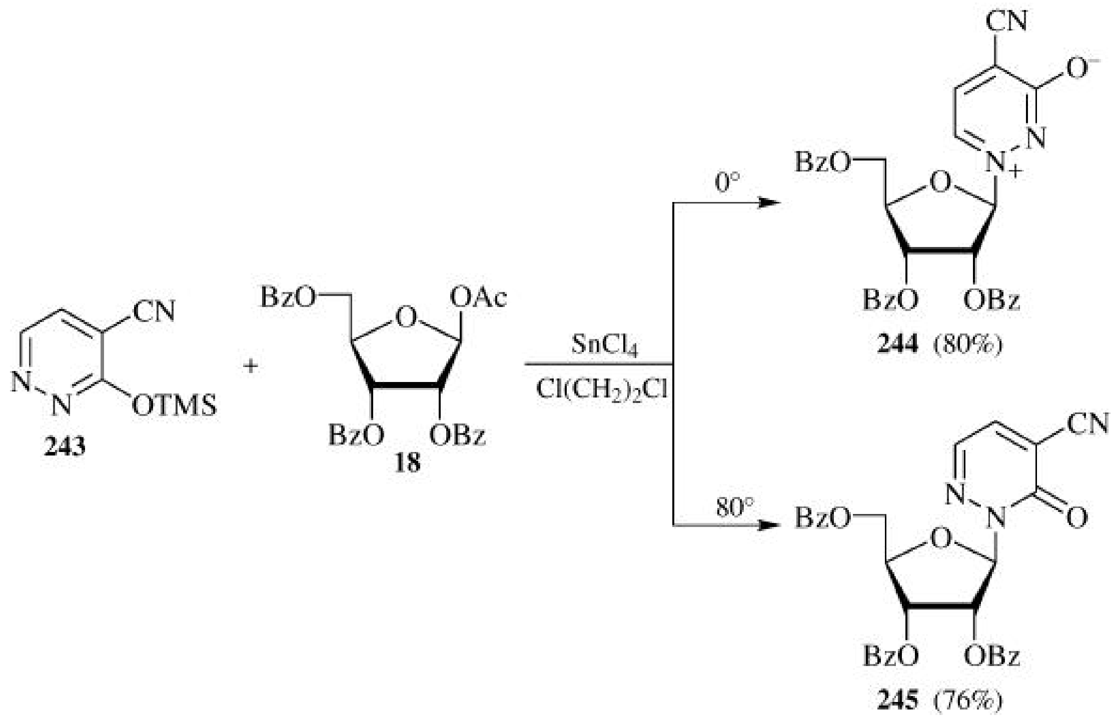
Reaction of silylated 4-cyano-2*H*-pyridazin-3-one **243** with **18** at 0° in the presence of $SnCl_4$ leads to the kinetically controlled rather stable mesoionic pyridazinium salt **244** (80%), which can be saponified to the free nucleoside. (253) Conducting the reaction of **243** with **18** and $SnCl_4$ at 80° or heating **243** with $SnCl_4$ in 1,2-dichloroethane affords the thermodynamically more stable nucleoside **245** in 76% yield. (253)



237 **238** **239**

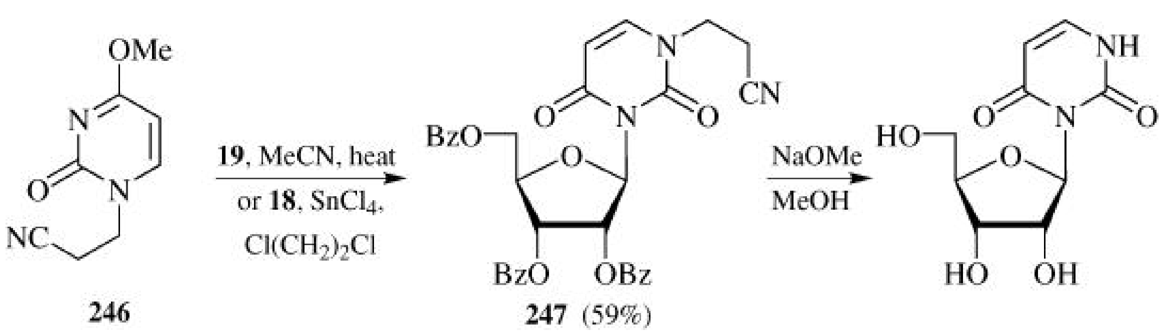


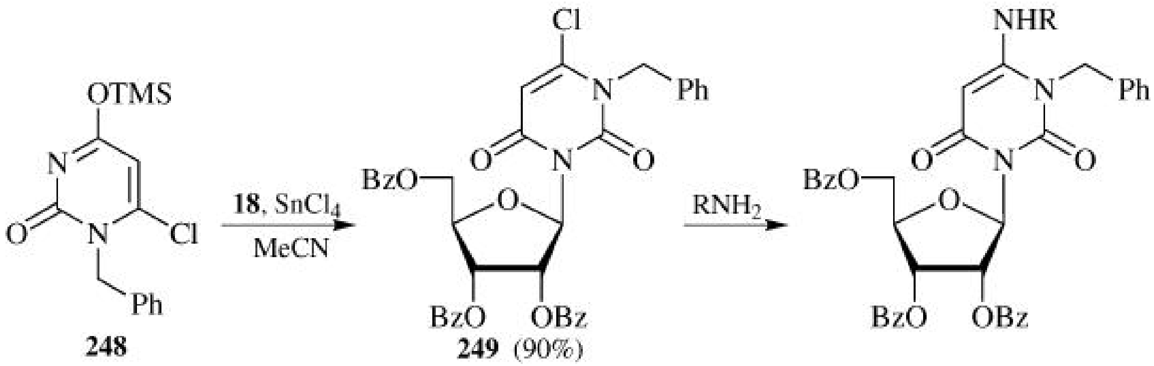
240 **241** **242**



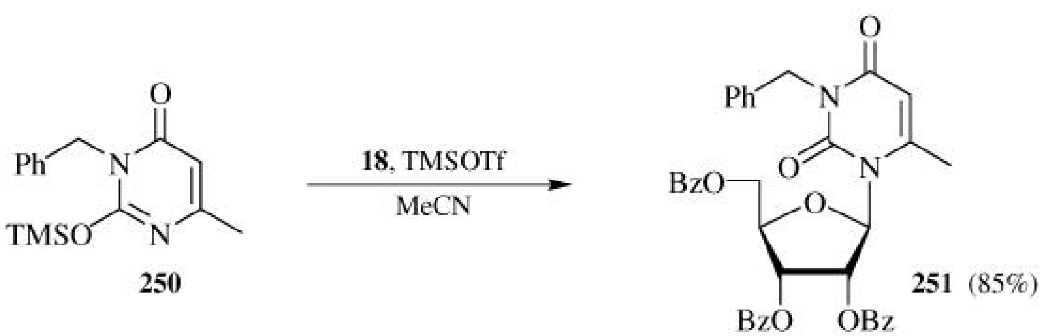
To add further complications, the presence of carbonyl or thiocarbonyl groups in these nitrogen heterocycles can lead to the corresponding *O*- or *S*-glycosides via kinetic control. Since these *O*- or *S*-glycosides are normally not observed on using thermodynamically controlled conditions in the presence of Friedel-Crafts catalysts, they are not dealt with here.

On blocking the 1 position of *O*-alkylated or *O*-silylated uracils by a β -cyanoethyl substituent, as in **246** or by a benzyl group as in **248**, exclusive N^3-substitution can be achieved. (254, 255) Alternatively, the silylated N^3-benzyl-6-methyluracil **250** reacts with the standard sugar **18** in the presence of TMSOTf in acetonitrile



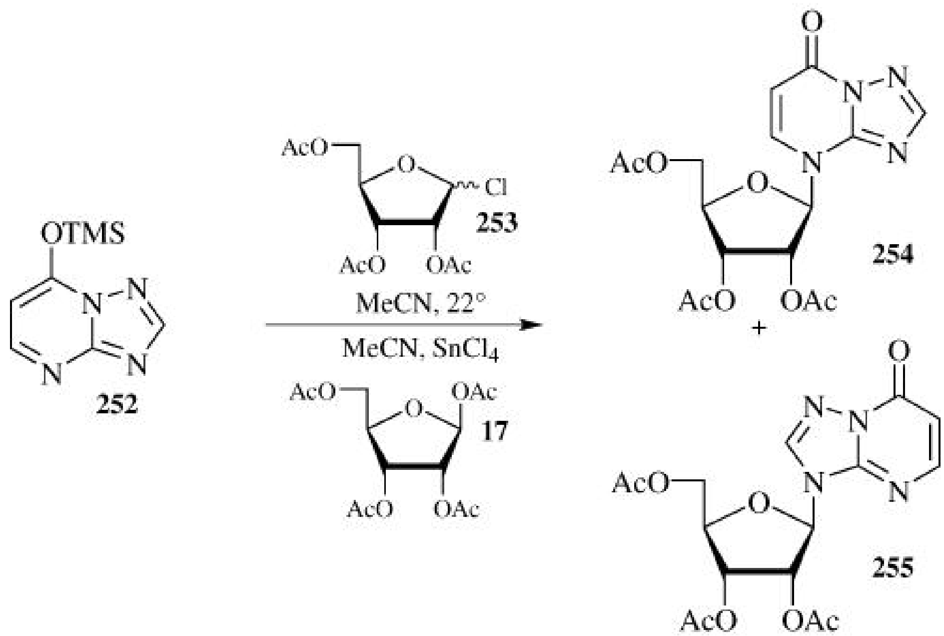


to give the protected 3-benzyl-6-methyluridine **251** (85%), from which the *N*-benzyl protecting group can be removed in 60% yield by treatment with BBr_3 (256) to give the protected 6-methyluridine **85**. For the application of the N^1-*n*-octylthiocarbonyl-blocking group, see Ref. 256a. Analogously silylated 3,6-



dimethyluracil or silylated 4-methylthio-6-methylpyrimidin-2-one afford the corresponding disubstituted uridines. (256)

The silylated heterocycle **252** reacts with 1-chlororibofuranose **253** in acetonitrile at room temperature to give a 3:2 mixture of **254** and **255** (38%), whereas its reaction with **17** in the presence of $SnCl_4$ affords an 84 : 16 mixture of **254** and **255** (55%). (257)



The sometimes complex regioselectivity observed with silylated imidazoles has already been discussed in the synthesis of protected bredinin (**218**). With 3-substituted 1,2,4-triazoles, the formation of N^1- or N^2-nucleosides can be only partially controlled. (133, 258, 259) Compare also the subsequently described reactions of benzotriazole **260** to give **261** and **262**. (271) Thus nucleoside formation of each new type of silylated heterocycle has to be investigated under a variety of reaction conditions to ascertain which conditions are optimal for the preparation of the kinetically or thermodynamically controlled nucleoside.

6. Special Preparations

6.1. Synthesis of 2′-Deoxynucleosides

Although the syntheses of 2′-deoxynucleosides from suitable derivatives of 2-deoxysugars and salts of acidic heterocyclic bases or silylated heterocyclic bases have already been discussed, the different methods for their preparation are summarized here. These syntheses are among the most difficult in nucleoside chemistry. There are three main problems:

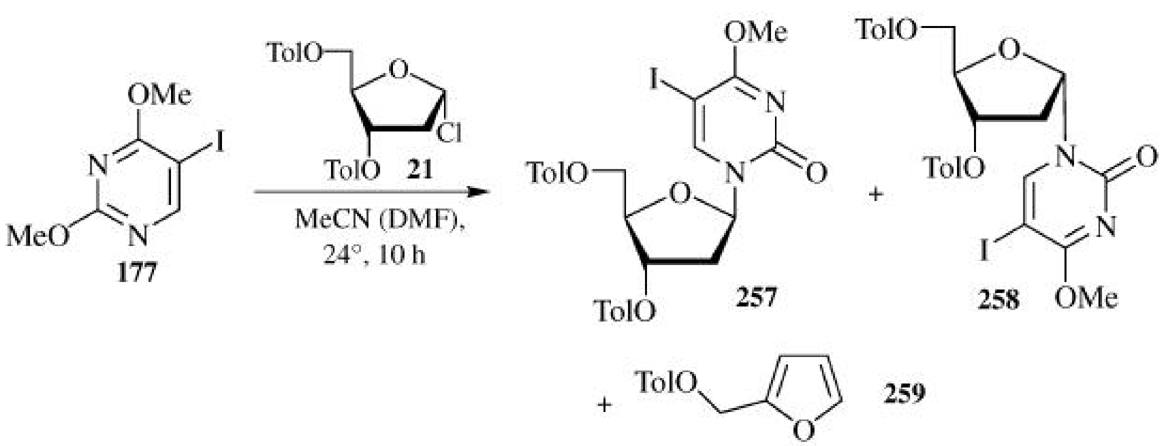
a. The derivatives of 2′-deoxysugars such as the commonly employed **21** are frequently rather unstable, although 1-alkoxysugars such as **119** are much more stable;

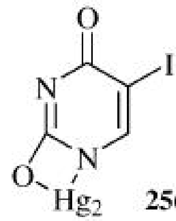
b. the total yields of the mixtures of the desired β anomer and the undesired α anomer are frequently only moderate; and

c. the ratios of the desired natural β anomer to the undesired αanomer are often difficult to control and to reproduce.

The standard sugar for the preparation of 2′-deoxyribonucleosides, the rather expensive crystalline **21** (prepared from **117** → **119** → **21**), is rather unstable. The 1- α -chloro moiety in **21** can isomerize, (260, 261) especially in polar solvents in the presence of Lewis acids or excess phase-transfer catalysts/ 50% NaOH, (262) to the 1- β -chlorosugar, which results in the formation of predominantly α -nucleosides.

Furthermore, **21** can eliminate hydrochloric acid as well as *p*-toluic acid to form the crystalline 2-(*p*-toluoyloxy)methylfuran **259** as described in the classical Hilbert-Johnson reaction, whereupon only 3% of the desired β -anomer **257**, 20% of the α -anomer **258**, and up to 27% of **259** are isolated. (263) The analogous reaction of 5-iodouracilmercury (**256**) with **21** in DMF gave only low yields of the corresponding α - and β -nucleosides but a large amount of **259**. (263)





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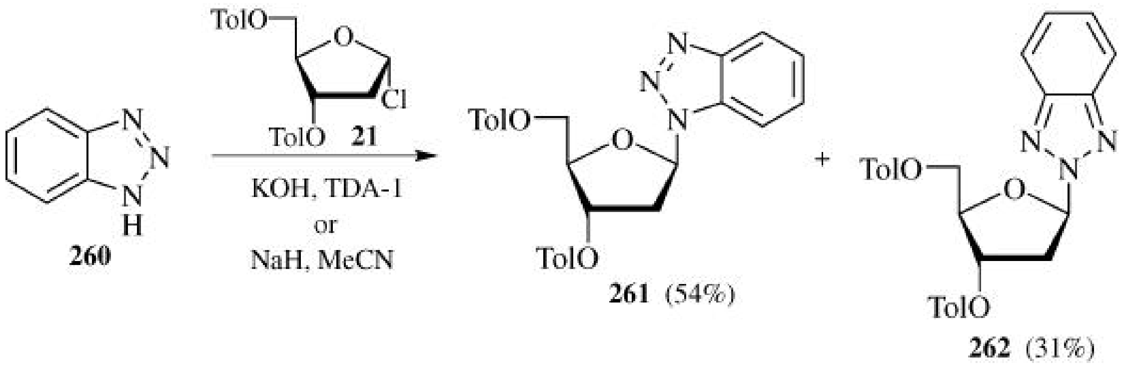
3′,5′-Di-*O*-*p*-toluoylated 2′-deoxy- β -nucleosides such as **257** or **123** crystallize better, melt at higher temperatures, are often less soluble than the corresponding α -nucleosides and can frequently be isolated by simple crystallization. In contrast, the corresponding 3′,5′-di-*O*-benzoylated, *p*-chloro-, or *p*-nitrobenzoylated derivatives often do not permit selective crystallization of the desired β anomer. (264-267)

The more acidic 3′,5′-*O*-acyl groups such as *p*-nitrobenzoyl, however, are much more readily removed by ammonia and primary or secondary amines than the *O*-*p*-toluoyl group. This can be of importance in the synthesis of nucleosides containing such base-sensitive groups as 5-trifluoromethyl. Thus only the 3′,5′ -di-*O*-*p*-nitrobenzoyl-2′-deoxy- β -D-ribofuranosyl-5-trifluoromethyluridine could be saponified selectively to the desired free nucleoside, whereas other acyl groups are hydrolyzed only under more vigorous conditions, which cause concomitant saponification of the 5-trifluoromethyl group to yield 2′ -deoxy-5-carboxyuridine. (268) Other investigators have used, however, the *p*-chlorobenzoate successfully to obtain, with sodium methylate and methanol, free 2-deoxy-5-trifluoromethyluridine. (269)

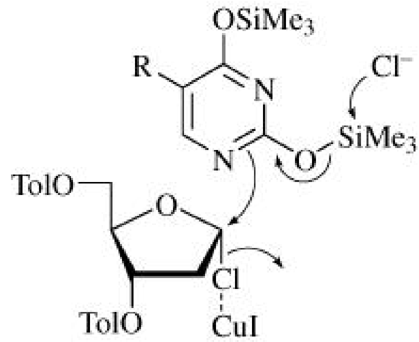
As described earlier, acidic heterocyclic systems such as 2,6-dichloropurine, 2,6-dichloro-4,6-imidazo[4,5-*c*]pyridine, 6-chloropurine, or even adenine form the sodium salts **40, 42**, or **45** on treatment with NaH in acetonitrile or acetone. These salts give on reaction with **21** nearly exclusively the desired β -nucleosides **41, 43**, and **46** (via S_N2 replacement of the 1 α chlorine) as well as N^7-nucleoside **44** and, in the case of **45**, α -nucleoside **47**.

Analogously, pyrrolopyridine **51** is converted in situ by KOH and the phase-transfer catalyst TDA-1 into the corresponding potassium salt, which reacts with **21** to afford the desired β -nucleoside **52** in 78% yield. (67) Powdered K_2CO_3/TDA-1 in acetonitrile often leads to considerably higher yields than standard phase-transfer conditions such as 50% $NaOH/Bu_4NHSO_4/CH_2Cl_2$. (270) Benzotriazole (**260**) analogously affords 54% of the N^1-nucleoside **261** as well as 31% of the N^2-nucleoside **262**. (271)



The Silyl-Hilbert-Johnson reaction of silylated substituted uracils and cytosines with the standard 1-halo-2-deoxysugar **21** in the presence of $HgBr_2$ or $AgClO_4$ furnishes the protected 2 -deoxynucleosides in moderate overall yields with α / β anomer ratios of 1:1–2. (80,272,272a)

The uncatalyzed as well as $ZnCl_2$-catalyzed reactions of silylated pyrimidines with **21** in anhydrous chloroform have been investigated. (261, 269) For example, the reaction of silylated thymine gave an α / β -ratio of 1:5 without catalyst. Importantly, the β -selectivity was increased in solvents with low dielectric constant, which promote S_N2 displacement while minimizing anomerization of the 1 α -chlorine. Catalysis by CuI in chloroform has been described (273) as promoting the formation of 90% of 2′-deoxypyrimidine nucleosides, favoring the β anomer over the α anomer by ratios of 9:1–9:3. These anomer ratios are seen even with the weakly nucleophilic silylated 5-nitrouracil, which reacts much slower than the more basic silylated uracils. (273-273a) A possible explanation for the β -selectivity and high yield of desired natural 2-deoxy- β -nucleoside might involve a push-pull process, in which nucleophilic attack of the silylated bases is assisted by CuI pulling at the α chlorine as depicted in **263**. This procedure has recently been applied successfully to reactions of silylated 6-azauracil and 5-methyl-6-azauracil with **21** to give the desired protected β -nucleosides in 70–75% yield, whereas silylated 5,6-dimethyluracil and **21** afforded the corresponding protected β -nucleoside in 50% yield. (274) For analogous reactions with CuCl in 1,2-dichloroethane, see Refs. 275, 275b. Addition of bases such as pyridine or triethylamine, as well as DBU, is reported to give an α / β ratio of 3:7 in reactions with 1-chloro-2,3-dideoxyribose derivatives. (276)



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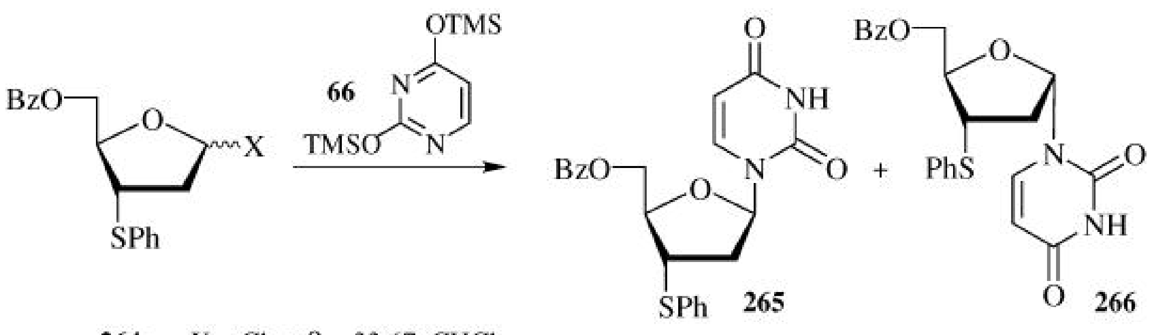
Pteridines have been reacted with 1- α -chloro-3,5-di-*O*-*p*-chlorobenzoyl-2-deoxyribofuranose in the presence of DBU to give the protected β -nucleosides in up to 54% yields. (276a)

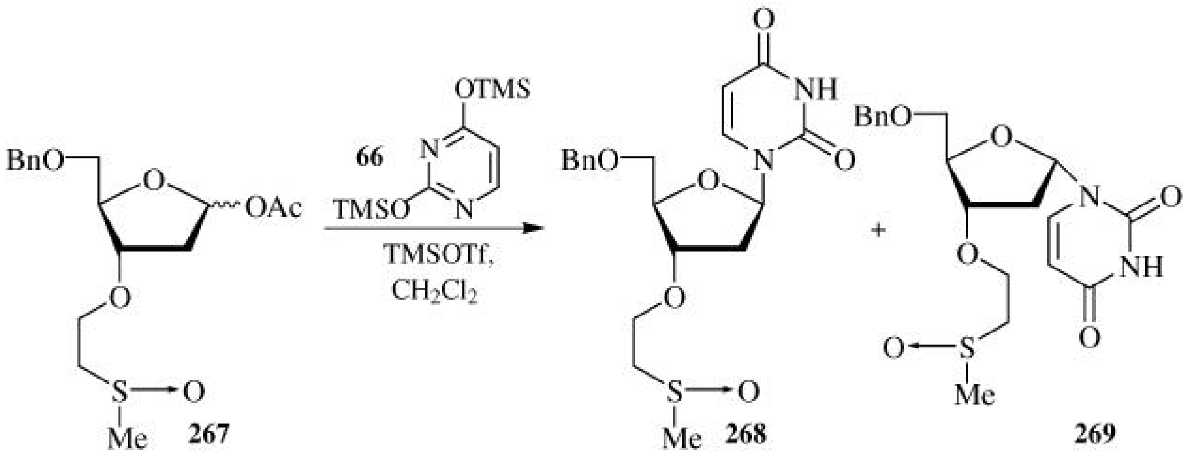
The uncatalyzed Silyl-Hilbert-Johnson reaction has been applied to an anomeric mixture (α : β = 33:67) of 1-chloro-2,3-dideoxy-3 α -phenylthio-5-*O*-benzoyl-D-ribose (**264a**) to give on reaction with silylated uracil **66** in chloroform an anomeric mixture of the nucleosides **265** and **266** in a ratio of 32:68 as anticipated by a S_N2 mechanism. (229) The corresponding mixture of 1-*O*-acetates **264b** reacts with **66** in the presence of $SnCl_4$ in CH_2Cl_2 to give **265** and **266** in a 69:31 ratio in 73% yield owing to the coordination of $SnCl_4$ with the sulfur atom in **264**, whereas TMSOTf affords a 40:60 ratio of **265/266** in 87% yield. (229)

The sugar moieties related to **264** with phenylthio (227–229,229a) or phenylselenyl (230, 230a,b) groups located at the 2 α position give primarily the β -nucleosides with silylated bases **66** or **226** in the presence of $SnCl_4$.



264a X = Cl α:β = 33:67, $CHCl_3$
264b X = OAc α:β = 31:69, CH_2Cl_2, $SnCl_4$

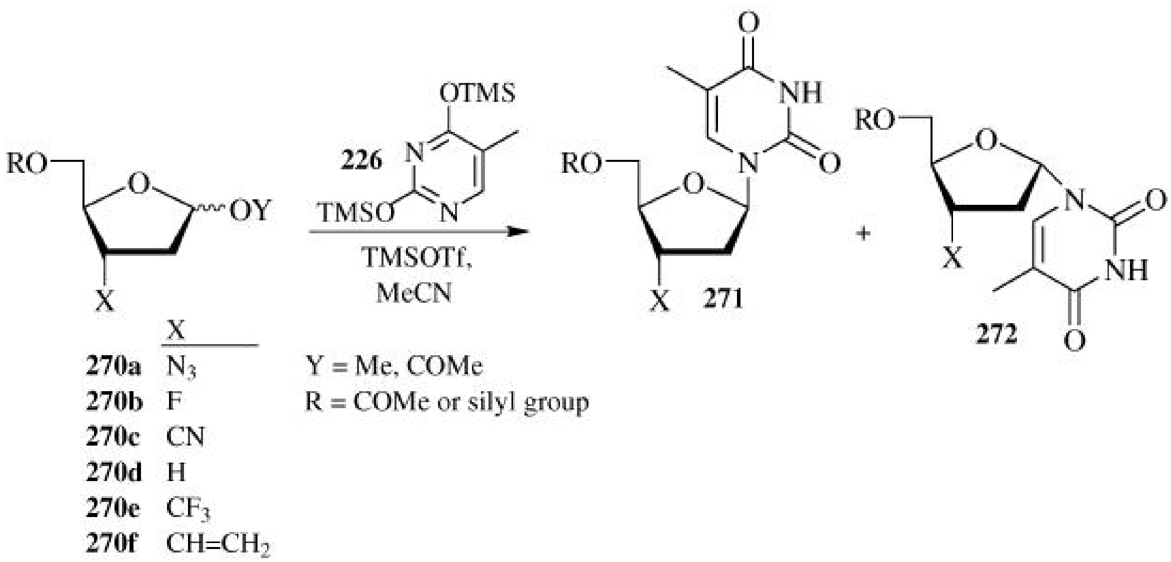
An analogous complexation with a Lewis acid involving a 3 α group is possible in sugar **267** to afford with **66** 90% of β -nucleoside **268** and the corresponding α anomer **269** in a ratio of 8:2. (277) As expected, a 3 α -methoxythiocarbonyl methylene group complexes even better with $SnCl_4$ than with TMSOTf (278) to give the corresponding β anomers in more than 90% yield with silylated cytosine or thymine and $SnCl_4$ as catalyst. [Also see 3 α -*O*-(*N*-benzoyl)carbamoyl derivatives, (278a) as well as 3 α -*O*- or 5-*O*-thiocarbamates, (278b,c) which control the trans stereochemistry.]



Since protected 1-halosugars such as crystalline **21** with an exclusively oriented 1 α halogen (or mesylate or tosylate) are usually not available, whereas the chemically stable precursors for the preparation of these derivatives are readily available, protected 1-*O*-methyl or 1-*O*-acetyl derivatives of 2-deoxysugars such as **119** have been commonly reacted with silylated bases in the presence of TMSOTf or $SnCl_4$ to give 1:1 mixtures of the α / β anomers in high yields. The variations in the α / β ratio between 6:4 to 4:6 as observed by many groups in the Friedel-Crafts-catalyzed synthesis of nucleosides, which probably proceeds primarily via an S_N1 pathway, might be due to the different basicities of the applied silylated bases and might furthermore reflect the thermodynamic stabilities of the anomers. Reacting methyl-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glycopyranoside in the one step–one pot version of the Silyl-Hilbert-Johnson reaction (HMDS/TMSCl/ $SnCl_4$ in CH_3CN) with silylated uracil , thymine, or N^4-benzoyl cytosine affords the protected nucleosides in high yield with an α / β ratio of ~ 1:3. (192)

In mixtures of peracylated 1-*O*-alkylfuranosides and pyranosides, the furanosides react via kinetic control at ambient temperature in the presence of TMSOTf in preference to the pyranosides. In addition, the undesired *O*-acylated and persilylated α -nucleosides (see **124** **123**) can be partially anomerized to the desired β -nucleosides in the presence of TMSOTf, thus raising the yields of the β -nucleosides. (133) The frequently obtained α / β ratio of 1:1 might also be due to the ready isomerization (anomerization) of the 4-*O*-trimethylsilylated intermediates in the presence of a Lewis acid such as TMSOTf, $SnCl_4$, and probably also $(NH_4)_2SO_4$. (151,152,152a) On heating 5 -*O*-(*tert*-butyldiphenylsilyl)thymidine with HMDS and 0.2 equivalent of $(NH_4)_2SO_4$ for 2 hours at 140°, the nucleoside bond is cleaved and 1,4-anhydro-2-deoxy-3,5-bis-*O*-(trimethylsilyl)-D-erythropent-1-enitol is isolated in 76% yield. (152a–c)

A series of 3 α -substituted 2-deoxysugars **270** was reacted with silylated thymine **226** in the presence of TMSOTf to give protected AZT **271a** (153, 279-286) or the related protected nucleosides **271b**, (288-291) **271c**, (114, 281, 287) **271d**, (276, 292-295) **271e**, (296) and **271f**, (297) as well as the corresponding α anomers **272**. For reviews of the preparation of these drugs, see Refs. 293-295.

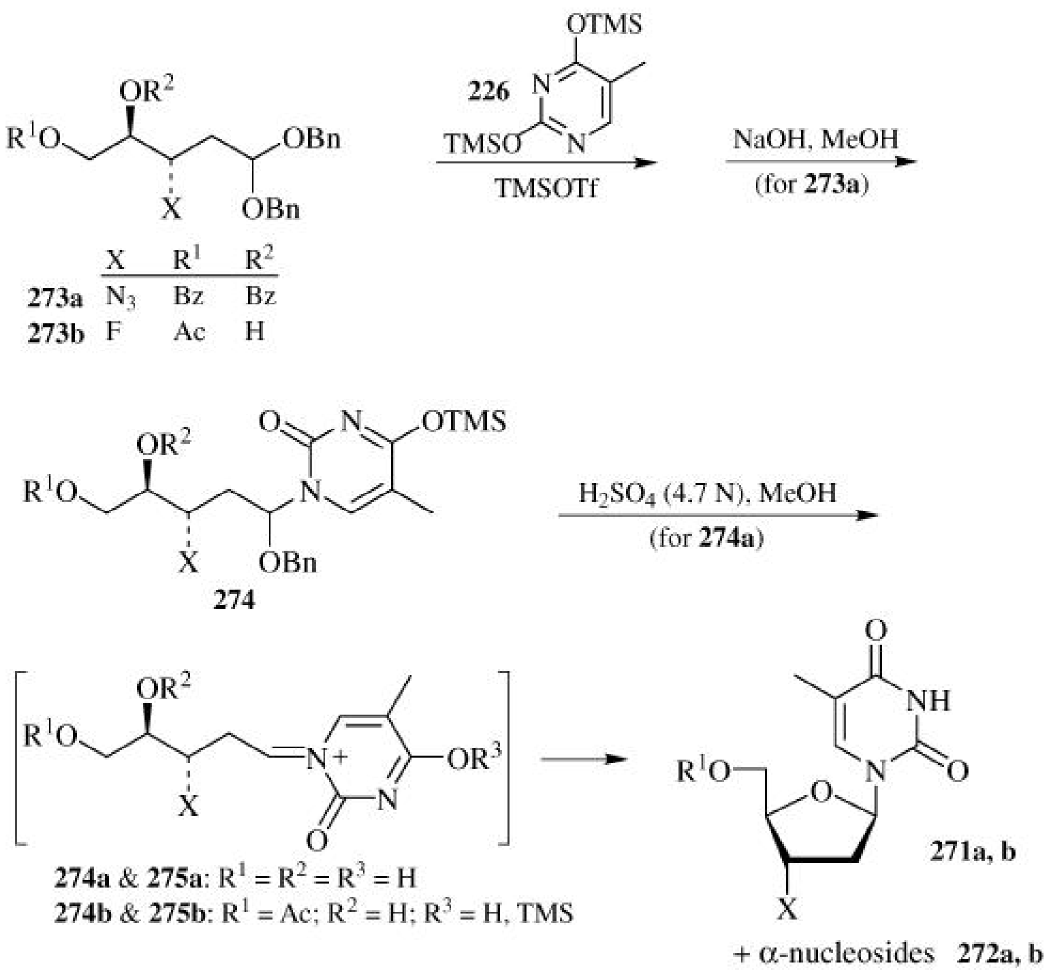


Analogously, **270d** reacts with silylated 6-chloropurine in the presence of TMSOTf in 1,2-dichloroethane to give an α / β = 1:1 mixture of the corresponding 2 ,3 -dideoxypurine nucleosides. (298) Interestingly, using Et_2AlCl instead of TMSOTf affords the α / β mixture of the desired N^9-nucleosides as well as the N^7-nucleosides. (298)

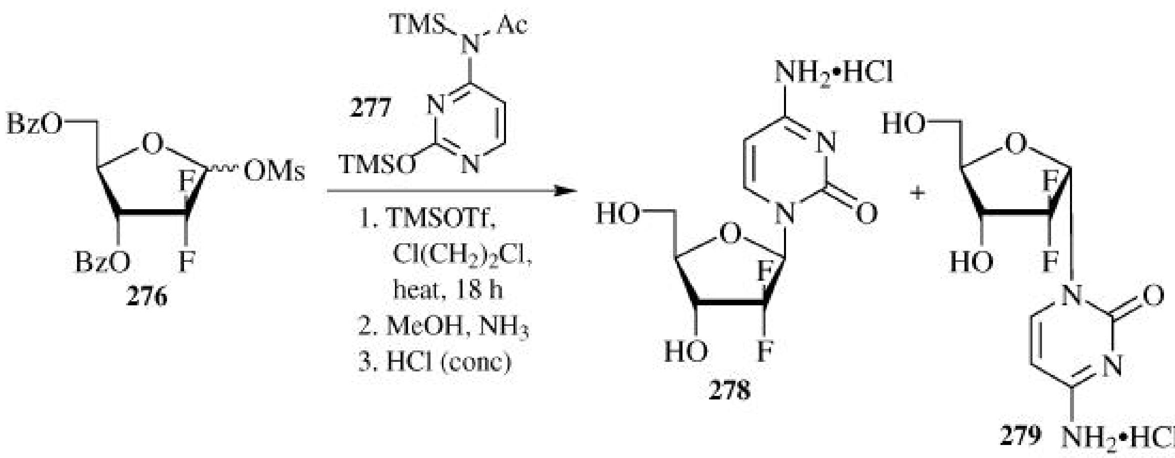
Starting from inexpensive noncarbohydrate precursors, Sharpless oxidation and subsequent reactions afford the optically active dibenzylacetals **273**, which react with silylated thymine **226** in the presence of TMSOTf to give seconucleosides **274**, which were isolated in the case of **274a**. Preferential acid-catalyzed cyclization of **274** via transition state **275** (gauche effect) affords exclusively or predominantly the anti-AIDS drugs AZT **271a** and **271b**, as well as small amounts of the corresponding α -nucleosides **272a** (299) and **272b**. (300)

As described subsequently in the section on the synthesis of arabinofuranosyl nucleosides, seconucleoside **332** analogous to **274** and **275** was isolated.

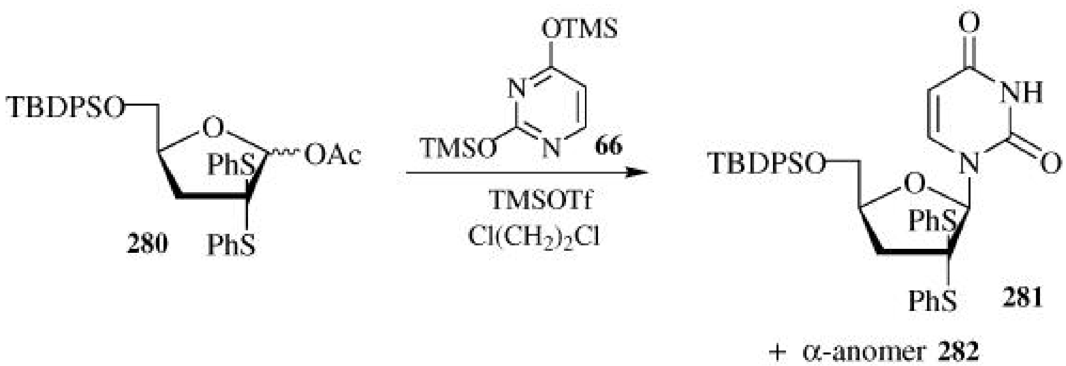
The synthesis of 2′-deoxy-2′,2′-difluorocytidine ("gemcitabine") **278** (301,301a,302) poses analogous problems. Reaction of the 2,2-difluoro-1-mesylate **276** with **277** in the presence of TMSOTf in 1,2-dichloroethane at reflux for 18 hours gives a crystalline 1:1 mixture of the hydrochlorides **278** and **279** in 49% yield. (302, 303) The α -nucleoside **279** can be anomerized to the β anomer **278** under basic conditions. (304) The two adjacent electron-attracting fluorine atoms, which deactivate any normal 1-acyloxy derivative, necessitate the 1-mesyloxy leaving group in **276** for a smooth reaction with TMSOTf to furnish the corresponding 1-cation.

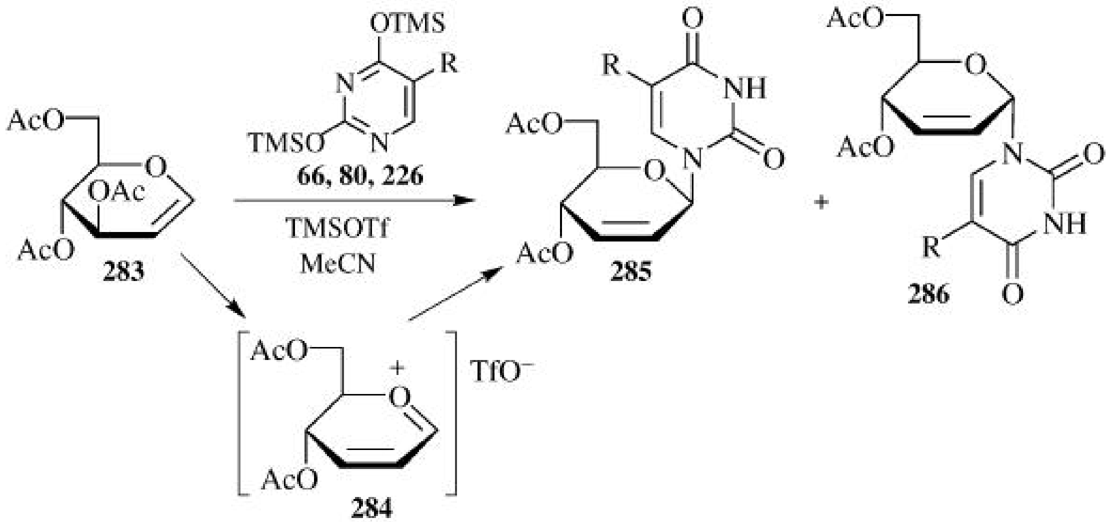


In contrast to the 2,2-difluorosugar **276**, the corresponding 1-*O*-acetyl-2,2-diphenylthiosugar **280** reacts with silylated uracil **66** in the presence of TMSOTf to furnish a 4:1 mixture of **281** and **282** in 83% yield. (305)



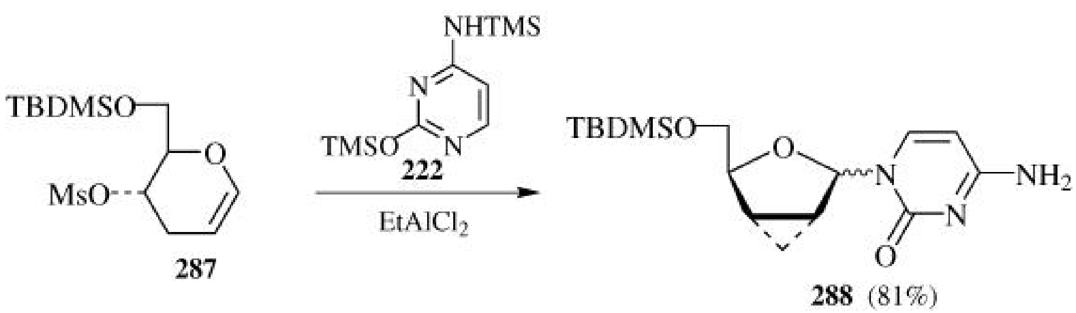
Acylated glucals such as 3,4,6-tri-*O*-acetyl-D-glucal **283** undergo a Ferrier reaction with Lewis acids (145) to yield conjugated cations such as **284** lacking an α- or β -directing group. The reactions of **283** with silylated uracils **66**, **80**, and **226**





in the presence of TMSOTf or $SnCl_4$ afford via **284** the 2′,3′-dideoxy-$\triangle^{2}$ nucleosides **285** and **286** in ~ 1:1 ratio in moderate yields. (306) Compare also other papers on these Ferrier-type (145) reactions. (307-312)

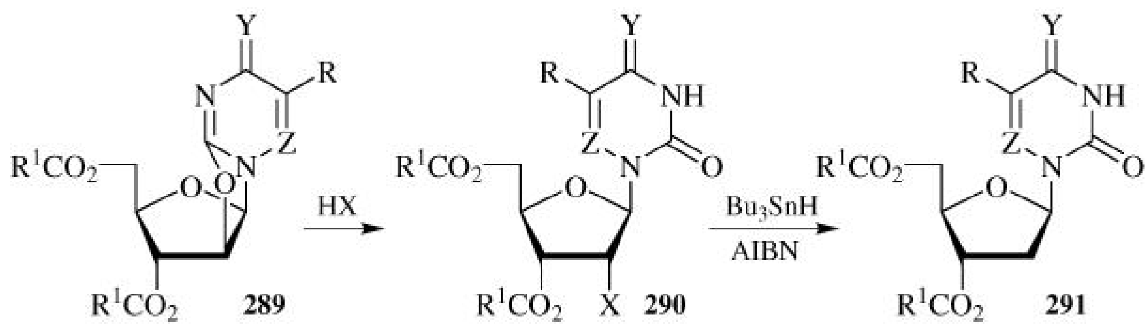
The homologous Ferrier reaction of mesylate **287** with disilylated cytosine **222** in the presence of $EtAlCl_2$ gives an α , β mixture of the cyclopropyl nucleosides **288** in 81% yield. (312a) An efficient Ferrier-type reaction was described employing *N,N*-dimethylformamide at reflux in the absence of a catalyst. (312b)



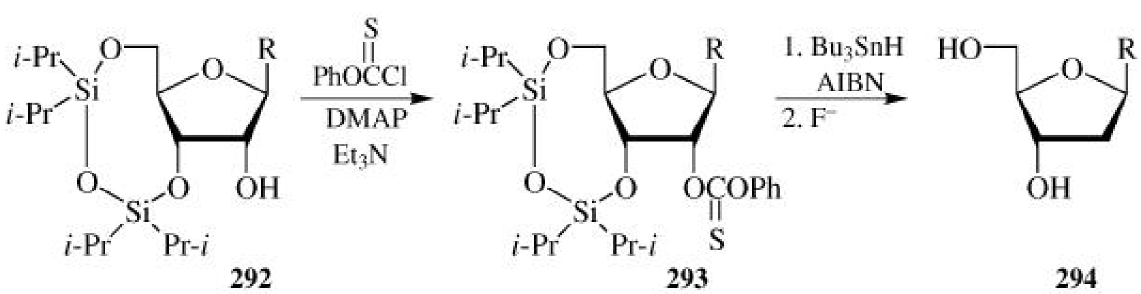
6.2. Chemical Conversion of Ribo- to 2 -Deoxyribonucleosides

As emphasized in the introduction, the building blocks of RNA—uridine, cytidine, adenosine, and guanosine—were apparently produced first during evolution and only subsequently reduced via their 5′-diphosphates by specific ribonucleotide reductases to the corresponding 2′-deoxynucleotides—the building blocks of DNA. Thus imitating nature, chemical methods have been developed to convert ribonucleosides into their corresponding 2′-deoxyribonucleosides.

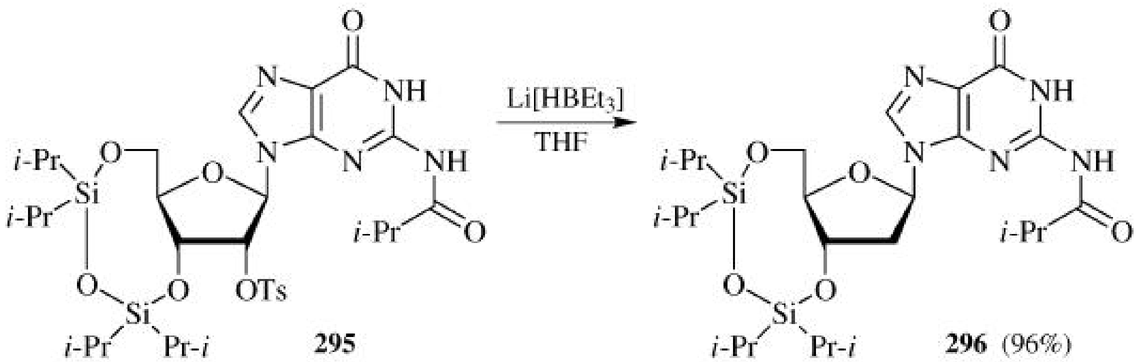
Uridine and cytidine as well as their 5-substituted or 6-aza analogs can be readily transformed into their corresponding 2′-deoxy-2′-halonucleosides **290** with acetyl bromide (313-317) or propionyl bromide (318, 319) in up to 94% yield via the protected 2,2′-anhydronucleosides **289**. The halogen atom X (Cl, Br) can subsequently be removed from **290** by hydrogenation (313, 318, 319, 321) or by Bu_3SnH–AIBN (315, 317) to give 2′-deoxynucleosides **291** in overall yields of up to 75%. Treatment with Zn or Zn/Cu (314, 316, 317) or electrochemical reduction (320, 321) leads to the 2′,3′-didehydronucleosides. Uridine or cytidine can also be treated first with methyl orthoacetate followed by acetyl bromide to give an even higher yield of the 2′-bromo intermediate **290**. (316, 317) Recently, 2′-*O*-(3-trifluoromethylbenzoyl-3′,5′-di-*O*-benzoates of nucleosides have been reduced photochemically in the presence of *N*-methylcarbazole to 2′-deoxynucleosides in up to 73% yields. (321a)



R = H, Me; Z = CH, N; Y = O, NH; R[1] = Me, Et; X = Cl, Br



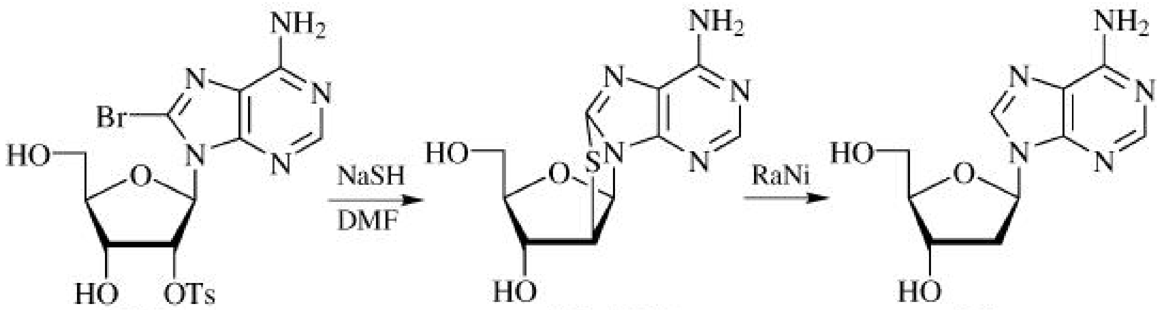
R = pyrimidine or purine base



Alternatively, the 3′,5′-hydroxy groups in ribo (or xylo) nucleosides as well as their analogs can be protected selectively by the bifunctional Markievicz reagent (322, 323) TIPS-Cl_2 to **292**, which are readily transformed by a Barton reaction via **293** to **294** in high overall yields. (324,324a,325) The intermediate radical at C-2′ can be trapped by allyltributylstannane to introduce a carbon substituent at the 2′ αposition. (326) The analogous protection of *N*[2]-isobutyrylguanosine and subsequent tosylation gives **295**, which can be reduced by Li($HBEt_3$) to **296** in 96% yield. (327) Furthermore, 2′-hydroxy-3′,5′-di-*O*-acetylribonucleosides can be obtained in up to 74% yield by selective saponification of the 2′-*O*-acetyl group in 2′,3′,5′-tri-*O*-acetates by hydrazine hydrate or hydroxylammonium acetate. (328, 329)

Both the 2′- as well as the 3 -hydroxy groups of ribonucleosides can be removed by either applying DMF-dimethylacetal (330,330a,331) or triethyl orthoformate (330) followed by heating with acetic anhydride, (330-330a) reaction with methyl iodide, (331) or by treatment of the 2′,3′-di-*O*-xanthates with Ph_2SiH_2 (332) to afford in high yields the 2′,3′-didehydronucleosides, which can be readily hydrogenated to the saturated nucleosides. Alternatively, reacting the ribonucleosides with 2-acetoxyisobutyryl chloride (333, 334) followed by treatment of the resulting mixture of 2′,3′-chloroacyloxy isomers with Zn/Cu-acetic acid also yields the corresponding 2′,3′-didehydronucleosides. (335,335a,b) The different synthetic strategies for the preparation of the anti-AIDS drug 2 ,3 -dideoxyinosine have been summarized. (336)

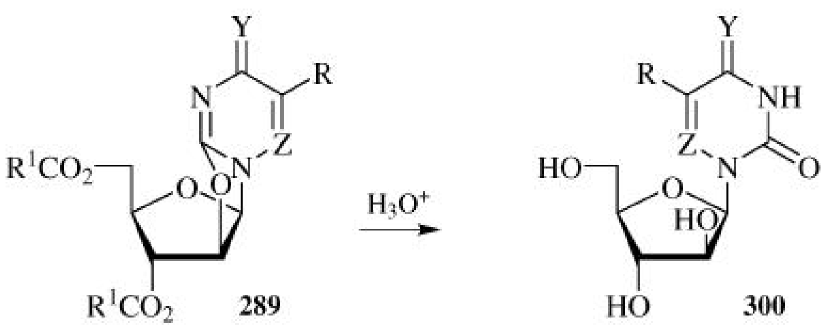
Starting with the readily available 8-bromopurine nucleosides, which are converted via the 2′,3′-dibutylstannylene derivatives to the corresponding 2′-*O*-tosyl derivatives such as **297**, heating with NaSH gives the 8,2′-*S*-cyclonucleoside **298** in 69% yield. Subsequent treatment with Ra-Ni affords 2 -deoxyadenosine (**299**). (337)



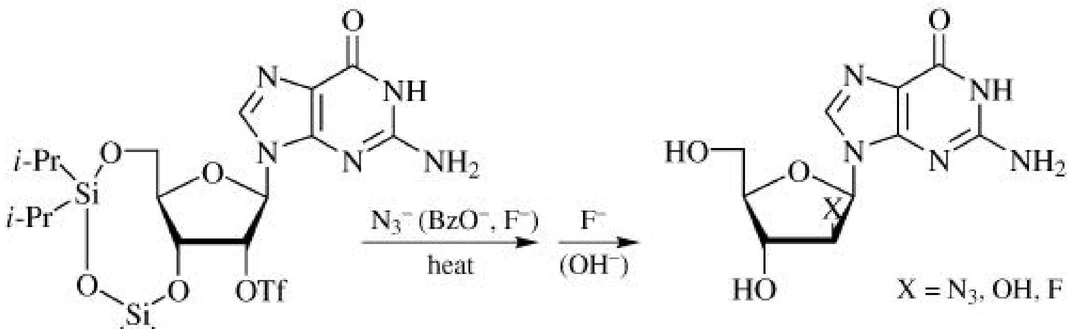
297 **298** (69%) **299**

6.3. Synthesis of β -D-Arabinofuranosylpyrimidine and Purine Nucleosides

Pyrimidine nucleosides can be readily converted into protected β -D-arabinofuranosylpyrimidine nucleosides **300** via 2,2′-anhydronucleosides **289** and subsequent hydrolysis. (338) Furthermore, β -D-arabinofuranosylpurine nucleosides **302** are accessible by S_N2 displacements of 2 -*O*-triflates of purine nucleosides **301** by azide, (339) benzoate, (339a,b) or fluoride ions (339c) followed by deprotection. But the total synthesis of β -D-arabinofuranosylpurine and -pyrimidine nucleosides is more complicated and of particular importance because of their interesting biological properties.

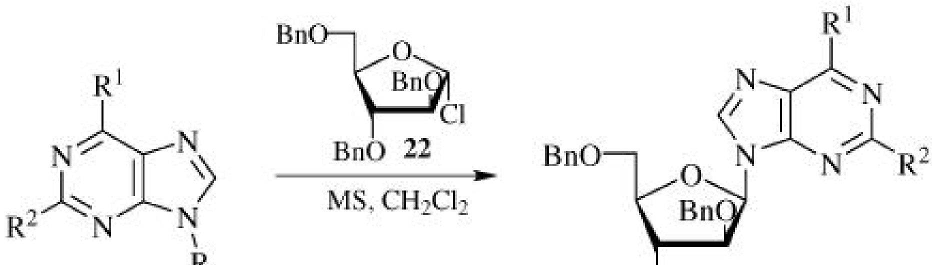


R = H, F; Z = CH, N; Y = O, NH; R[1] = Me, Ph



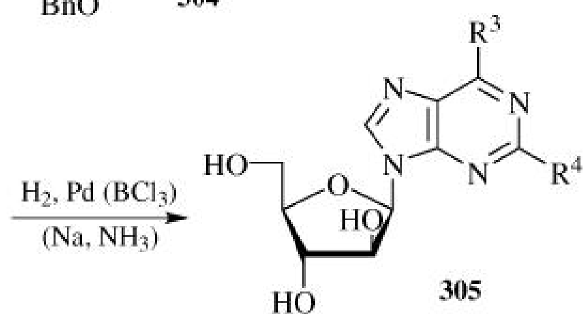
301 302

In the first synthesis of such a nucleoside, *N*[6]-benzoyladenine **303a** was reacted with the standard 2,3,5-*O*-benzyl-D-arabinofuranosyl chloride (**22**), (52, 53) which consists of more than 90% of the 1 α -chloro derivative, (340) in the presence of molecular sieves to give **304a** in 46% yield. (341) Hydrogenation of **304a** affords free 9- β -D-arabinofuranosyladenosine **305a** in more than 90% yield. (341)



303 304

	R	R[1]	R[2]	R[3]	R[4]
a	H	NHBz	H	NH_2	H
b	H	OH	NHAc	OH	NH_2
c	H	Cl	NHAc	Cl	NH_2
d	H	Cl	Cl	Cl	Cl
e	H	NHAc	NHAc	NH_2	NH_2
f	TMS	NHTMS	NHTMS	NH_2	NH_2
g	H	NH_2	F	NH_2	F
h	H	Cl	F	Cl	F
i	H	OH	Cl	OH	Cl

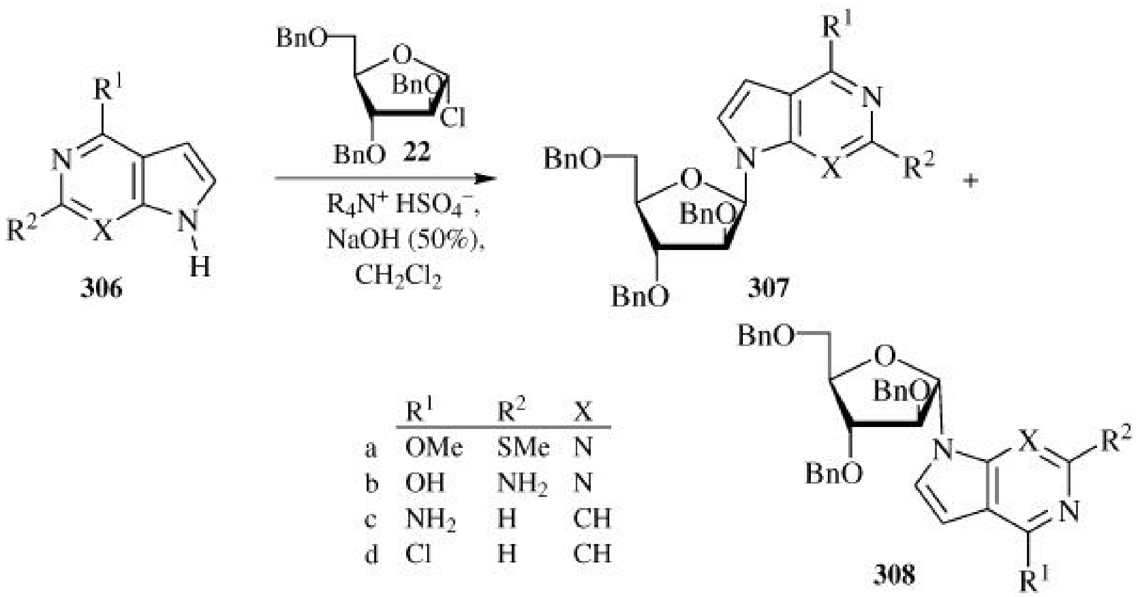


305

Subsequent studies established that the reactions of 2,6-disubstituted purines **303** with **22** proceeded to **304** in ~ 50% yield in nonpolar solvents in the presence of molecular sieves, (341-343) whereas with $Hg(CN)_2$ as catalyst the formation of the corresponding α -nucleoside (α / β = 2.5:1) was favored. (343) In the reaction of 2,6-diacylaminopurine **303e** or the silylated base **303f** with **22**, the addition of molecular sieves, (342-345) distillative removal of TMSCl, (346) or addition of diisopropylethylamine (347) are recommended.

The benzyl ether groups in **304** can be readily removed by BCl_3, (344, 345) by hydrogenation with H_2/Pd, (341, 342, 347) or by treatment with sodium in liquid ammonia (343) to give the corresponding free nucleosides **305**.

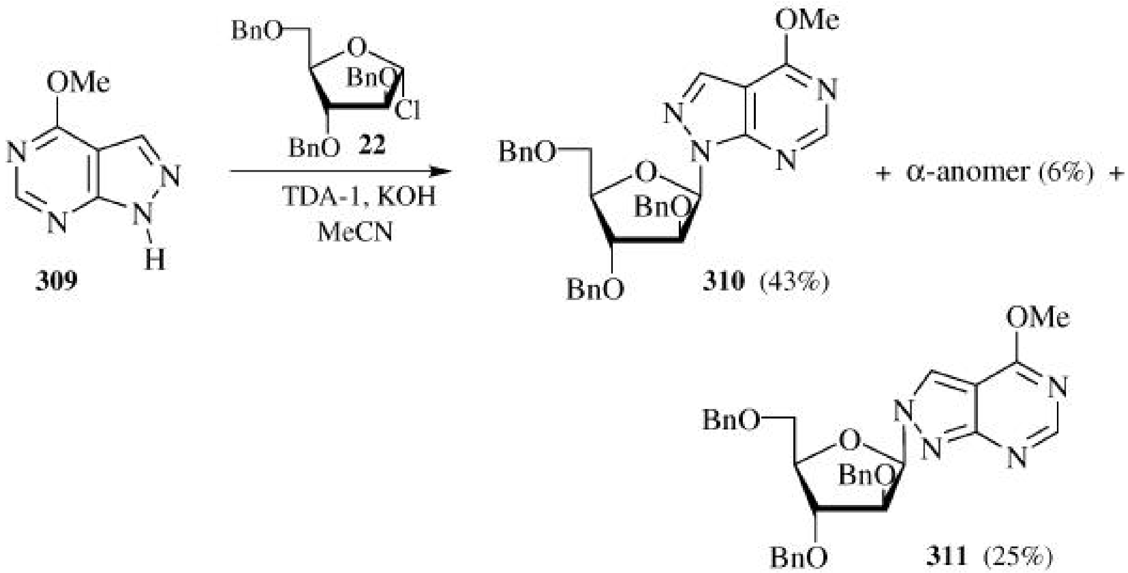
Alternatively, the acidic 7- and 3,7-deaza analogs (348, 349) **306** and **22** are readily converted in the presence of phase-transfer catalysts predominantly into the corresponding β -nucleosides **307** and some α -nucleosides **308**. Interestingly, the concentrations of the phase-transfer catalyst (348) and NaOH (66, 349) influence the ratio of **307** to **308**. A lower concentration of the phase-transfer catalyst tetrabutylammonium hydrogen sulfate (0.2 molar versus 1 molar) favors formation of the β anomer **307**. (348) The 1 α -chlorine in **22**, which is displaced in a S_N2 reaction by the *N*-anion of **306**, apparently undergoes equilibration at higher concentrations of tetrabutylammonium hydroxide to give more of the 1 β -chloride and consequently more of the corresponding α -nucleoside **308** (cf also the preparation of **49** and **50** (66, 67)).



	R^1	R^2	X
a	OMe	SMe	N
b	OH	NH_2	N
c	NH_2	H	CH
d	Cl	H	CH

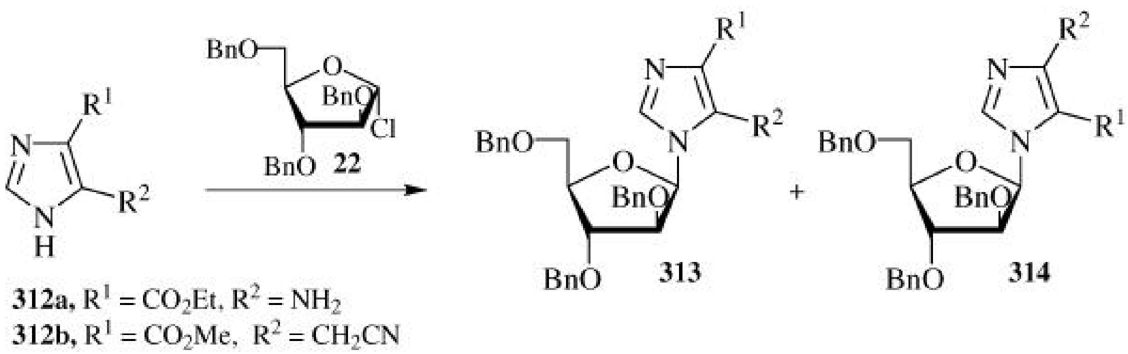
Reaction of pyrazolopyrimidine **309** with **22** furnishes 43% of nucleoside **310**, 25% of the isomeric **311**, and 6% of the α anomer of **310**. (340) Imidazo[4,5-*d*]-isothiazoles give mixtures of the corresponding N^4- and N^6-regioisomers in good yields. (350)

The reaction of free or silylated imidazoles **312** with **22** proceeds with **312a** to give ~ 30% of **313a** in the presence of triethylamine in CH_3CN , (351-353) whereas

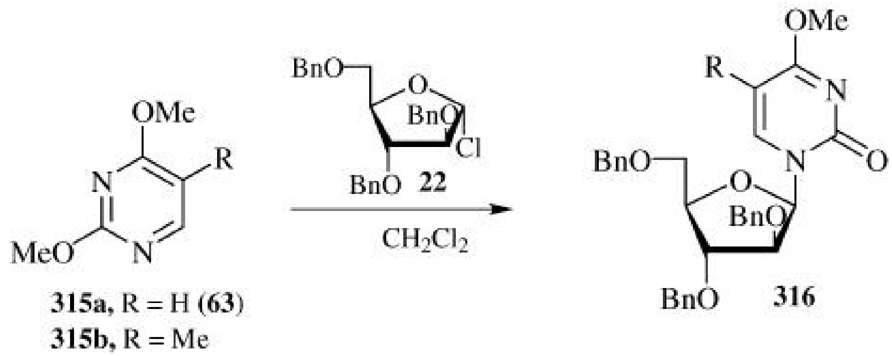


312b affords predominantly **314b** as well as nucleoside **313b** after pretreatment with NaH in DMF. (354)

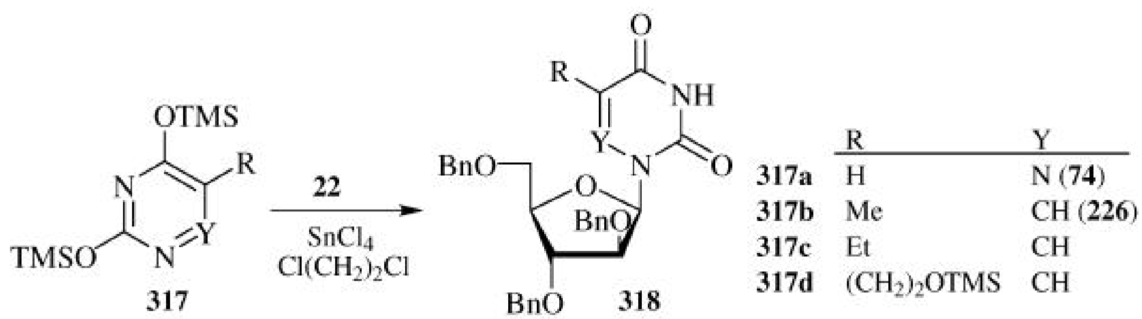
After conversion to the sodium salt with NaH/ CH_3CN , 2-carbomethoxy-3-cyanopyrrole reacts with **22** to give the corresponding β -D-aranucleoside **313** in 59% yield. (355)



After unsatisfactory reactions of 2,4-dimethoxypyrimidine **315a** (**63**) with **22** (356) to give **316a**, the 5-methyl derivative **315b** reacted with **22** in CH_2Cl_2 to give **316b** in 49% yield. (357) See also the reaction of 2,4-diethoxy-5-ethylpyrimidine with **22** to afford 80% of the corresponding 4-ethoxy-5-ethyl analog of **316**. (358)

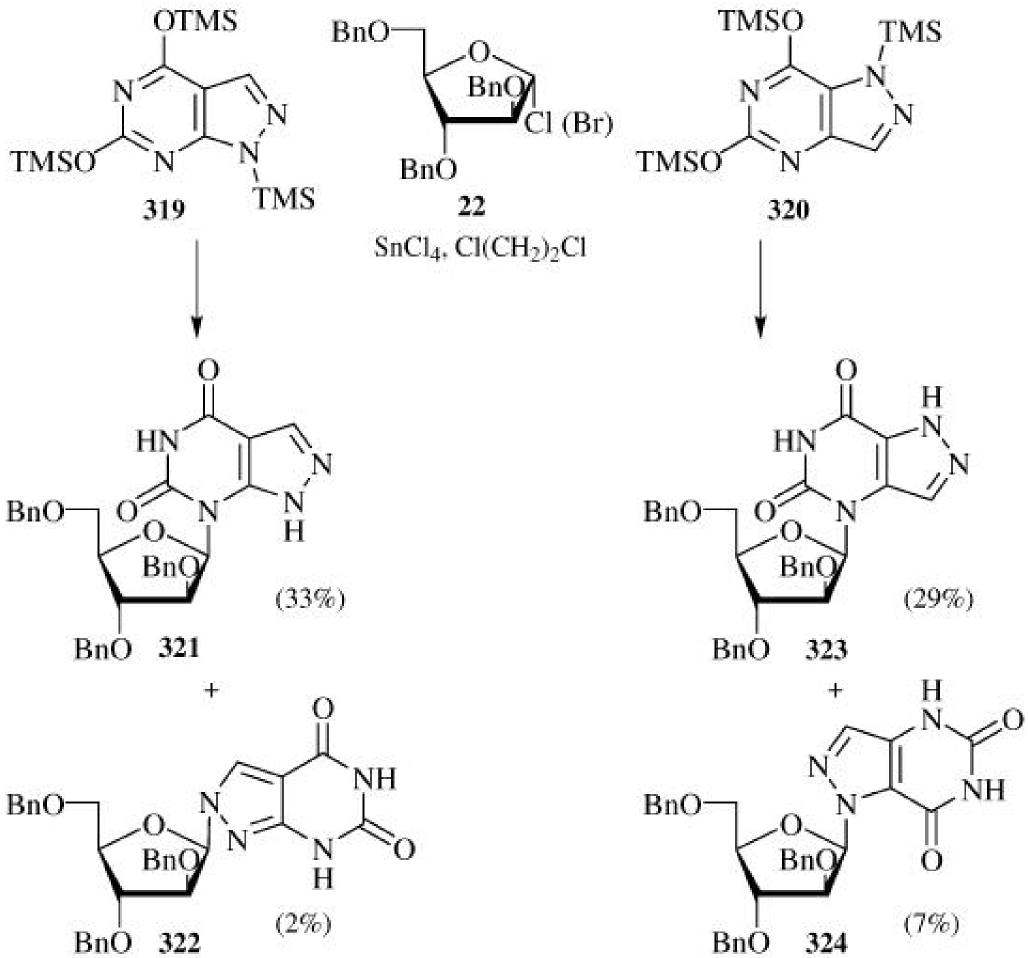


Silylated pyrimidines **317b–c** or 1,2,4-triazine **317a** react with **22** in 1,2-dichloroethane and $SnCl_4$ (84, 358, 359, 363) to give β -nucleosides **318** in 40–60% yield. The analogous reaction of **317d** with **22** in CH_2Cl_2 and molecular sieves affords β -nucleoside **318d** in 58% yield. (360)

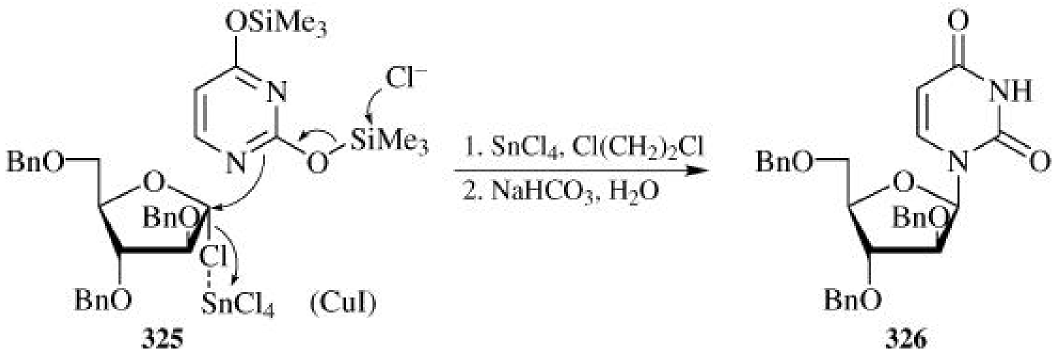


The silylated pyrazolouracils **319** (361) and **320** (362) react analogously with **22** in the presence of $SnCl_4$ as catalyst to give the corresponding β -nucleosides **321** and **323** as well as the isomeric β -nucleosides **322** and **324**.

The formation of ara- β -nucleosides **318, 321–324** is surprising since a 2 β -alkoxy group can coordinate with $SnCl_4$ and stabilize a cation at position 1 on

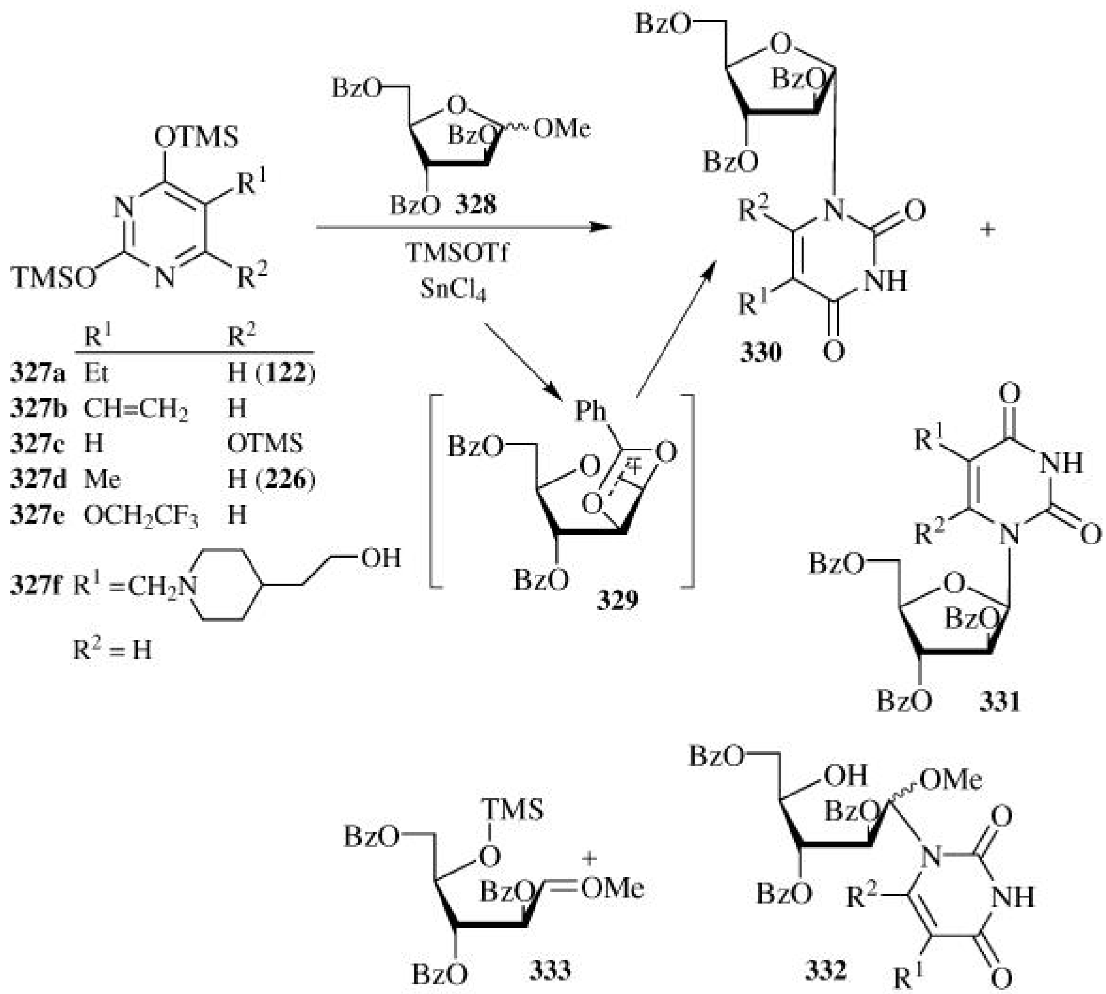


the β side to result in the preponderant formation of the corresponding α -nucleosides. Thus it was demonstrated that reaction of 1-*O*-acetyl-3,5-di-*O*-benzoyl-2-*O*-methyl- β -D-ribofuranose with silylated uracil in the presence of $SnCl_4$ or TMSOTf (226b) afforded primarily the desired natural 2′-*O*-methyl-3,5-di-*O*-benzoyl- β-uridine. (225,226,226b) Reaction of a 2 α -*tert*-butyldimethylsilyloxyribose derivative with silylated uracil and $SnCl_4$ furnished primarily the β -nucleoside. (226-226a) It is possible that $SnCl_4$ assists in the S_N2 reaction of the silylated base by coordination to the 1 α -halogen from the α side as depicted in **325**. As a consequence, gradual addition of $SnCl_4$ (or of **22**) under diminished pressure in 1,2-dichloroethane (to remove the trimethylsilyl chloride formed) might give rise to increased amounts of the β -anomer **326**. The potential influence of CuI in an analogous reaction of silylated bases with **22** as indicated in **325** should also be considered.

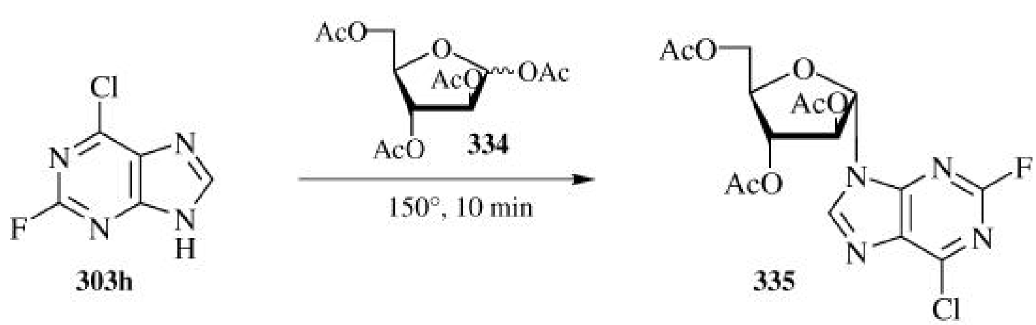


Silylated uracils **327** react with peracylated derivatives of D-arabinose **328** in the presence of $SnCl_4$ or TMSOTf via intermediate **329** in accordance with the Baker rule (205) to furnish exclusively the α-aranucleosides **330** (358, 364-366) (see also a corresponding pyranose example (367) as well as a reaction with silylated theophyllin (368)). There is only one exception described: the reaction of **327e** with **328** in the presence of $SnCl_4$ in CH_2Cl_2 is claimed to give the β -nucleoside **331e** in 57% yield. (369)

Condensing **327d** with **328** in the presence of one equivalent of TMSOTf at 0° in acetonitrile provides (via **329**) 63% of the anticipated α -nucleoside **330d** as well as the crystalline seconucleoside **332d** in 3% yield, whereas **327f**, which contains a basic side chain, neutralizes the catalyst TMSOTf, giving a ~ 50% yield of the crystalline seconucleoside **332f**. Addition of excess catalyst TMSOTf to the reaction mixture leads to the anticipated ring closure of the persilylated seconucleosides **332** to **330**. (370) The formation of **332** is envisioned to take place by addition of TMSOTf to the furanoside oxygen atom in methyl 2,3,5-tri-*O*-benzoyl- α -D-arabinofuranoside **328** to give the intermediate secocation **333**, which reacts with the silylated bases **327** to give seconucleosides **332**. (370) Recently, on reaction of methyl 2,3-dideoxy-3-fluoro-5-(4-phenylbenzoyl)- β -D-erythropentafuranoside with silylated thymine **226** in the presence of TMSOTf in acetonitrile at – 25° a seconucleoside corresponding to **332** was isolated in 21% yield. The authors postulated that the aforediscussed addition of TMSOTf to the furanoside oxygen is a general reaction resulting in secocations such as **333**. (370a) For further examples leading to analogous seconucleosides employing 1-*O*-methyl-3,5-di-*O*-*p*-toluoyl-2-deoxyribofuranoside **119** and other sugars in the presence of $SnCl_4$, see references (370b–f). On treatment of 3′,5′-diacetylthymidine with acetic anhydride/H_2SO_4 in acetonitrile, anomerization as well as formation of acetylated seconucleosides was observed. (152-152a)

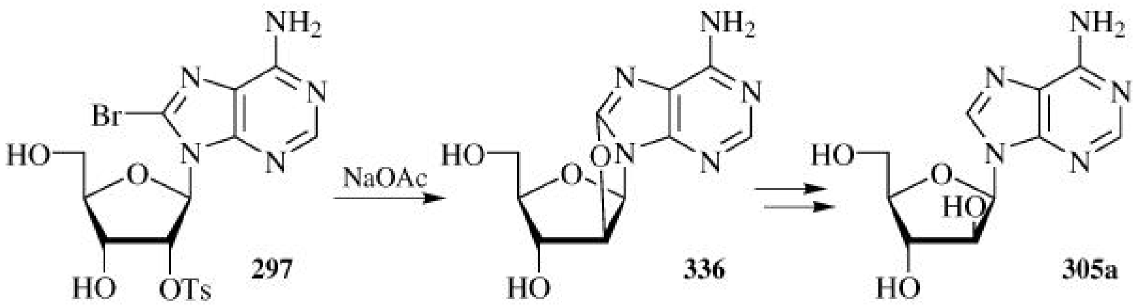


On fusion of 1,2,3,5-tetra-*O*-acetyl-D-arabinofuranose **334** with the acidic 2-fluoro-6-chloropurine **303h** at 150°, 85% of the anticipated α -nucleoside **335** is obtained. (343)



Apart from the hydrolysis of anhydronucleosides **289** to arapyrimidine nucleosides **300**, the Walden inversion of 3′,5′-*O*-protected 2′-*O*-triflates such as **301** with acetate or benzoate anions gives the corresponding 2′-*O*-acylated β -arabinofuranosylpurine nucleosides, and after hydrolysis araguanosine **302b** (X = OH). Because of the difficulties in preparing arapurine nucleosides with the expensive **22**, conversion of purine nucleosides such as guanosine (**5**) into arapurine nucleosides **303** should preferably be carried out via 3,5-protected 2′-*O*-triflates **301**. (339-339b)

Reaction of 8-bromo-2′-*O*-tosyladenosine (**297**) with sodium acetate in acetic acid/acetic anhydride followed by heating with sodium acetate in DMF affords the cyclonucleoside **336**, which is cleaved with hydrazine to lead to araadenosine (**305a**) after oxidative removal of the 8-hydrazino group with HgO. Araguanosine (**305b**) can be prepared analogously. (371)

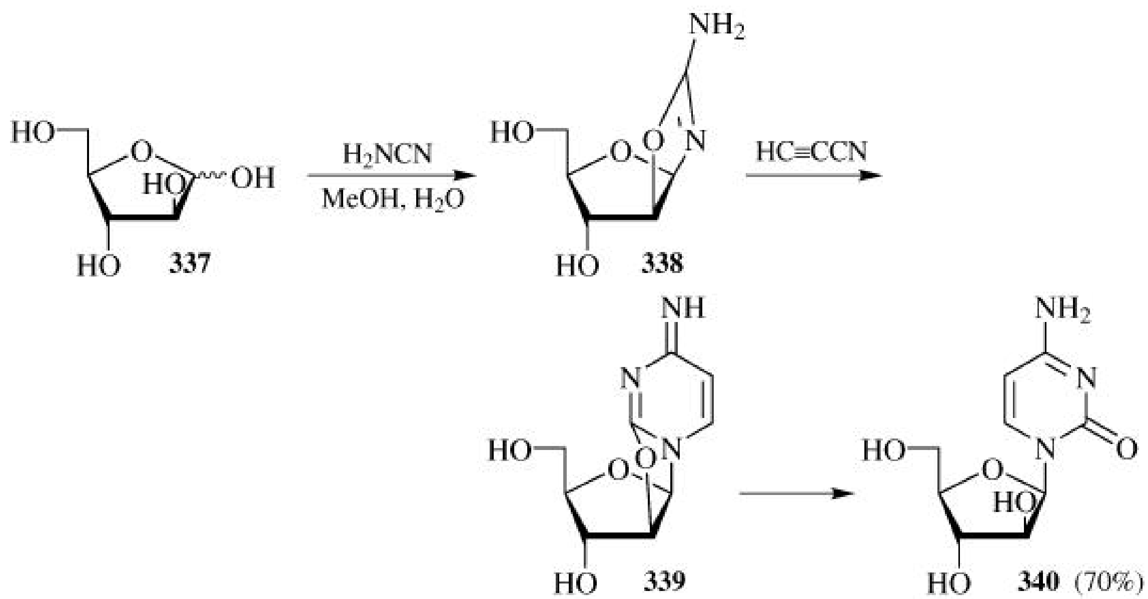


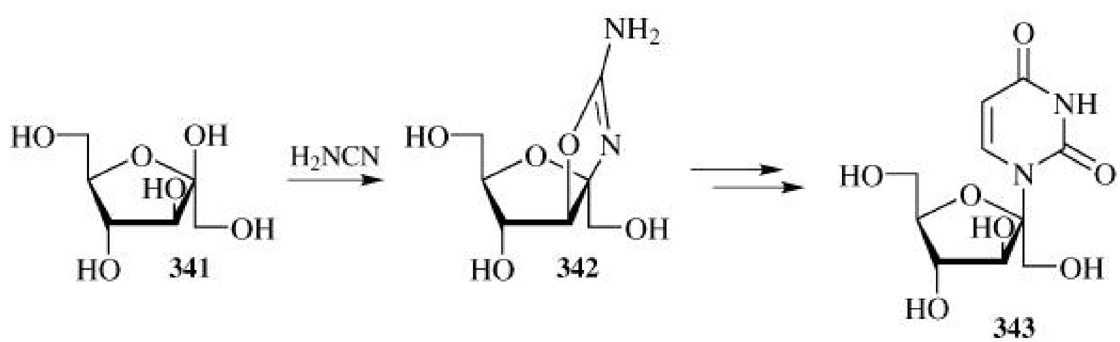
A different approach to the synthesis of β -D-arabinopyrimidine nucleosides is the prebiotic type-synthesis of aracytidine (**340**). On heating D-arabinose (**337**) with cyanamide in aqueous methanol to 50°, the crystalline oxazoline **338** can be isolated in up to 70% yields. (372-374) Subsequent reaction of **338** with cyanoacetylene and hydrolysis with aqueous ammonia leads via **339** to β -D-arabinofuranosylcytosine (aracytosine) (**340**) in up to 70% yields. (372-374) A modified approach gives rise to arauridine (375, 376) or arathymidine (377) as well as to 2′-deoxy-2′-chloro-6-methyluridine. (378, 379)

In a similar fashion, condensation of D-fructose (**341**) with cyanamide affords the oxazoline **342**, which is converted via 2,2 -anhydronucleoside and mild hydrolysis to 1-(β -D-fructofuranosyl)uracil **343**. (380, 381)

The synthesis of purine aranucleosides by enzymatic transglycosylation starting from uracil or cytosine arabinosides (382-382a) is discussed subsequently.

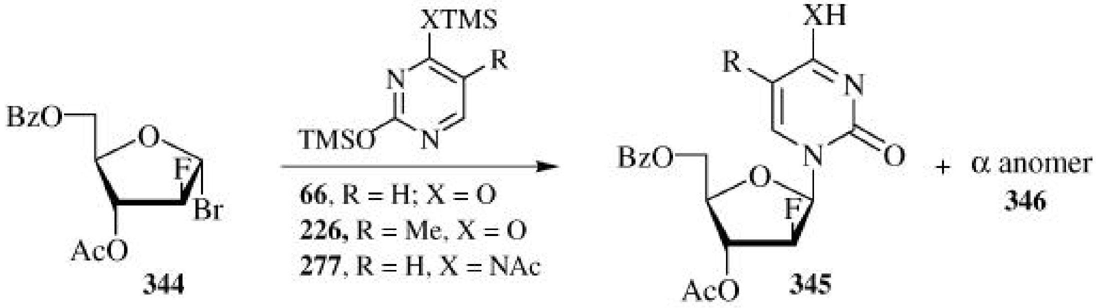
The synthesis of 2′-fluoro-2′-deoxy- β -D-arabinofuranosyl nucleosides is fraught with problems similar to those observed in the synthesis of β -D-arabinonucleosides. Whereas the conversion of 3′,5′-*O*-protected 2′-*O*-triflates such as **301** with fluoride anions to the corresponding 2′-fluoro-2′-deoxy- β -D-arabinofuranosyl nucleosides **302** (X = F) has already been mentioned, such nucleosides can also be synthesized by reaction of 2-fluorosugar **344** with silylated pyrimidine bases **66**, **226**, or **277**. These reactions proceed in CH_2Cl_2 for 4 days at 24°, (383) in acetonitrile in the presence of TMSOTf, (360) in CH_2Cl_2 in the presence of $Hg(CN)_2$ (383a) at 24°, at 40° with molecular sieves, (384) in boiling chloroform, (385, 386) or



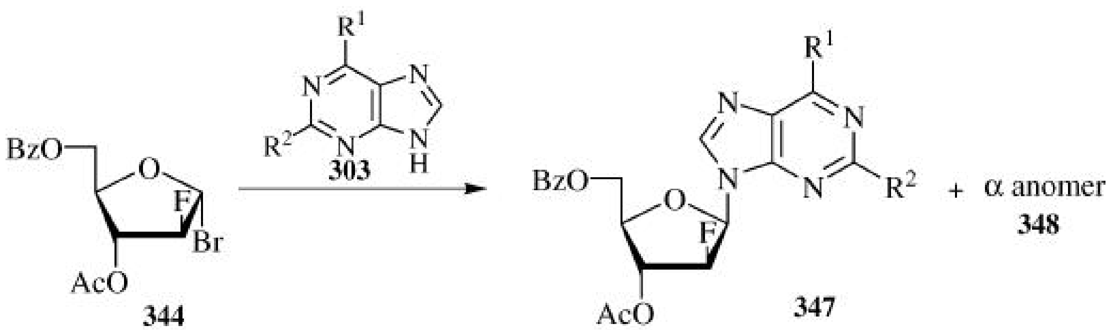


in the presence of NaI in CH_2Cl_2/ CH_3CN (387) to give the desired β-nucleosides **345** and the α -nucleosides **346** in up to 60% yield with α / β ratios of up to 1:20. Analogous reactions of silylated 2-pyrimidone and its 5-fluoro analog with **344** in 1,2-dichloroethane at reflux are also described, (388) as are reactions of silylated pyrimidines, (389, 390) cytosine, and free (391) or silylated 6-chloropurine (390-392) with the corresponding arabino- or

3-deoxysugar in the presence of TMSOTf (**102**). (392) For a mechanistic discussion of these reactions, see Ref. 385.



Reaction of N^6-benzoyladenine (**303a** = **137**) with **344** for 3 days in CH_2Cl_2 at reflux in the presence of molecular sieves affords **347** (R^1 = NHBz;R^2 = H)



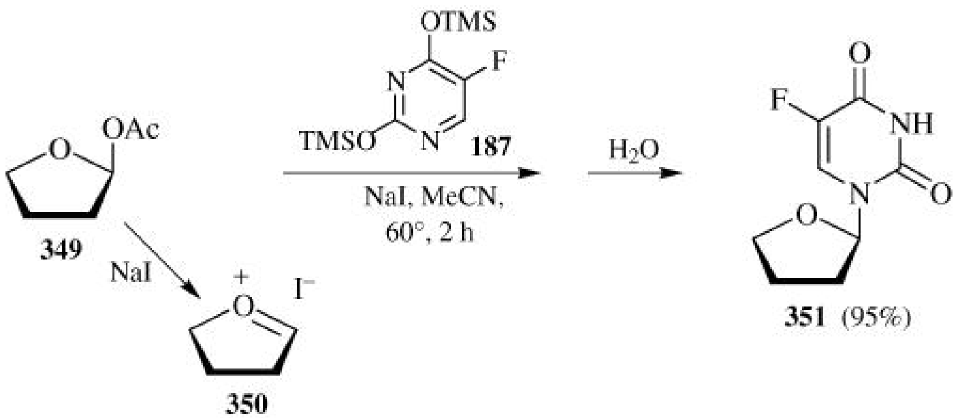
in 34% yield, as well as the α anomer **348**, (384) whereas silylated 2-acetamido-6-chloropurine (**303c**) in benzene at reflux for 4 hours in the presence of $Hg(CN)_2$ furnishes **347** (R^1 = Cl;R^2 = NHAc) in 32% yield. (384) Reaction of N^6-methyladenine with NaH in DMF followed by addition of **344** affords ~ 40% of **347** (R^1 = $NHCH_3$;R^2 = H). (298) Analogous reaction of 6-chloropurine with NaH in CH_3CN followed by **344** gives ~ 70% of **347** (R^1 = Cl;R^2 = H) as well as the corresponding α anomer **348** and minor amounts of the N^7 anomers. (393)

7. Miscellaneous Methods

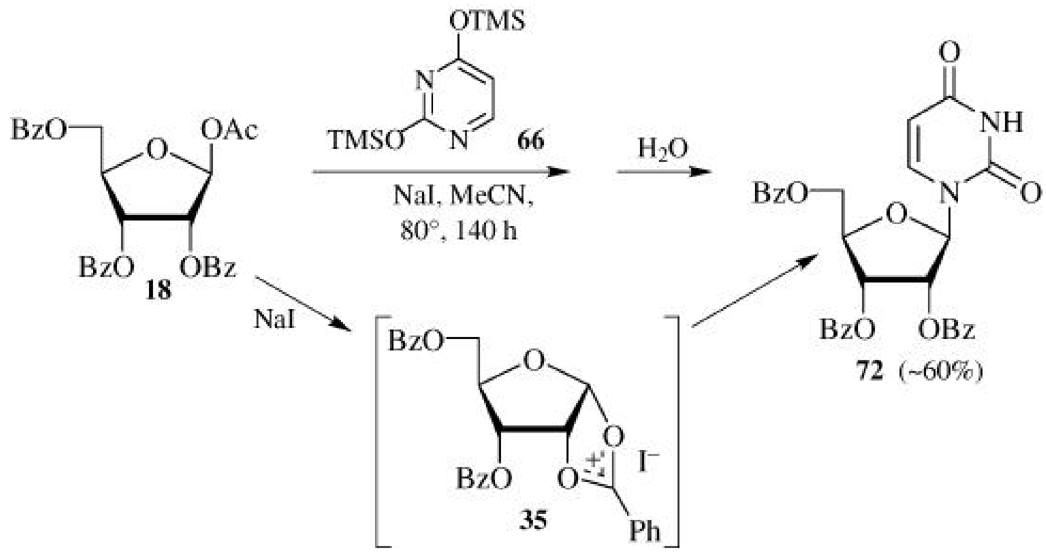
7.1. Alternative Silyl-Hilbert-Johnson Procedures

7.1.1. Catalysis by Alkali Halides

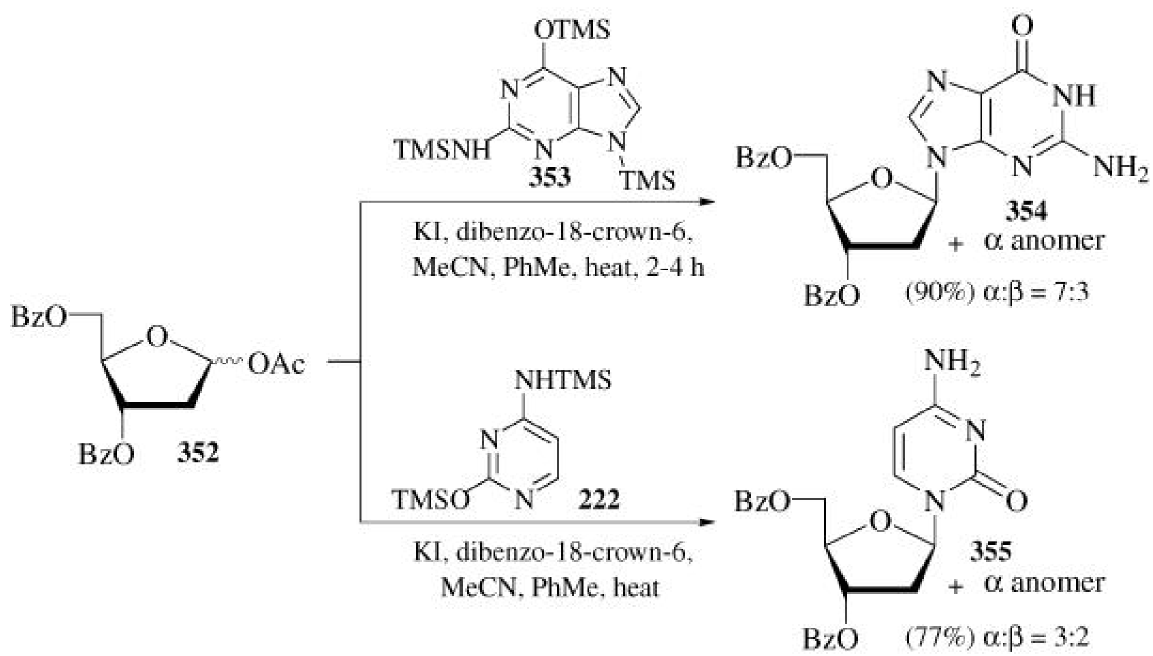
A patent describes the smooth reaction of 2-acetoxytetrahydrofuran **349** with silylated 5-fluorouracil **187** in the presence of sodium iodide to give via **350** the anticancer drug Ftafur® **351** in 95% yield. (394) In the analogous reaction of the stable standard sugar **18** with silylated uracil **66** much more drastic reaction conditions are required to afford the *O*-benzoylated uridine **72** in ~ 60% yield via **35**. (395)



It should be realized, however, that condensation of the reactive sugar intermediates **350** and **35** (iodide counterion) with the silylated bases **187** and **66** generates trimethylsilyl iodide, which is an effective Friedel-Crafts catalyst in nucleoside synthesis. Subsequently, potassium iodide/dibenzo-18-crown-6 as catalyst was used in the reaction of the 2-deoxysugar **352** with the silylated bases



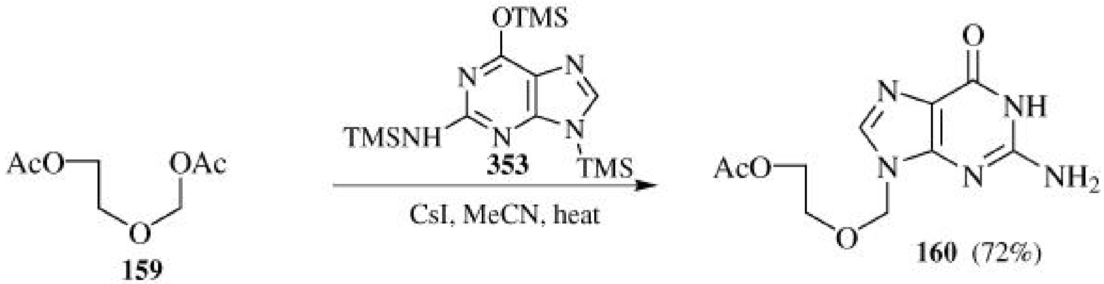
353 and **222** in acetonitrile:toluene (1:1) to give nucleosides **354** and **355** in 70–90% yield. (396) Nucleosides of secosugars were prepared analogously. (397, 398)



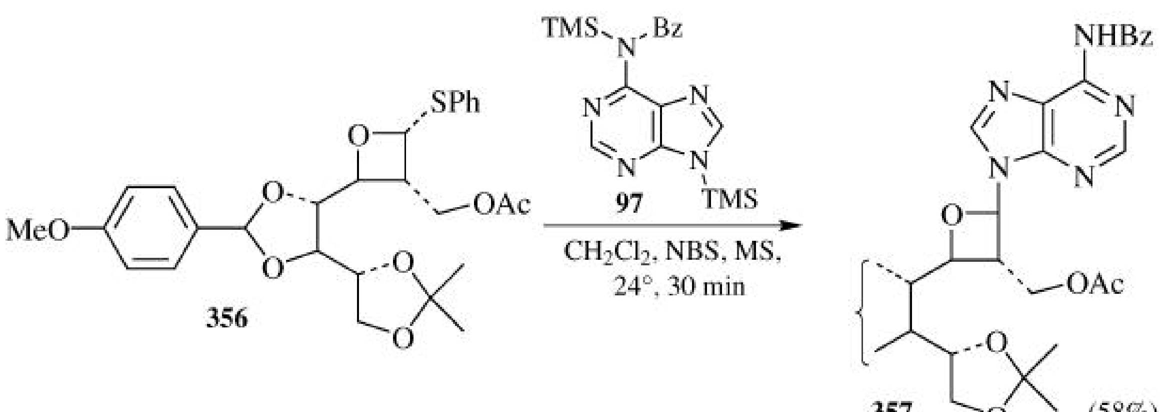
Silylated bases such as silylated thymine **226** or silylated guanine **353** react with the secosugar **159** in the presence of CsI in acetonitrile at reflux to afford **160** in 47% yield. (399, 400) In addition to NaI, KI, and CsI, CsCl is also effective in the reaction of 2-acetoxytetrahydrofuran (**349**) with silylated 5-fluorouracil **187**, furnishing **351** in 87% yield. (401)

7.1.2. Activation of 1-Sulfur Groups

Parallel to publications on the activation of protected alkyl 1-thio sugars by *N*-iodosuccinimide (NIS) (402) in the presence of catalytic amounts of trifluoromethanesulfonic acid (TfOH) for glycoside synthesis,



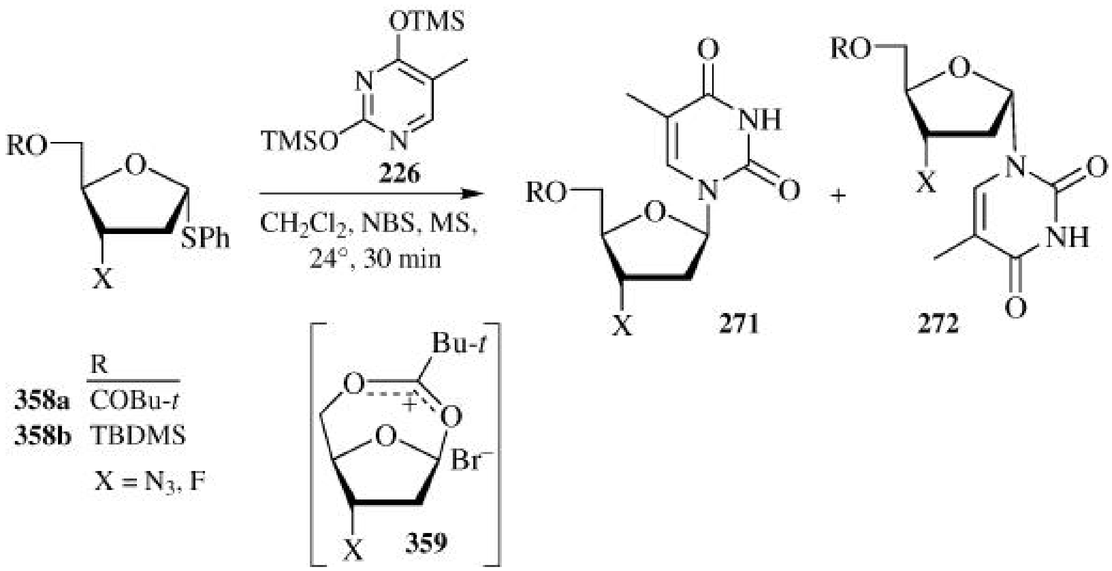
earlier studies showed that 1-phenylthiooxetane sugar derivative **356** reacts in CH_2Cl_2 with silylated N^6-benzoyladenine (**97**) in the presence of *N*-bromosuccinimide (NBS) and molecular sieves (4 Å) to give oxetanocin intermediate **357** in 58% yield. (403) The 1-phenylthio derivatives are often prepared via protected 1-*O*-acyl derivatives employing trimethylsilylated thiophenol in the presence of $BF_3{\cdot}OEt_2$ or TMSOTf. (410) Thus the question arises, why not use the protected 1-*O*-acyl or 1-*O*-alkyl sugars for nucleoside synthesis instead of the corresponding 1-phenylthio sugars, which entail additional reaction steps and bad smelling thiophenols.

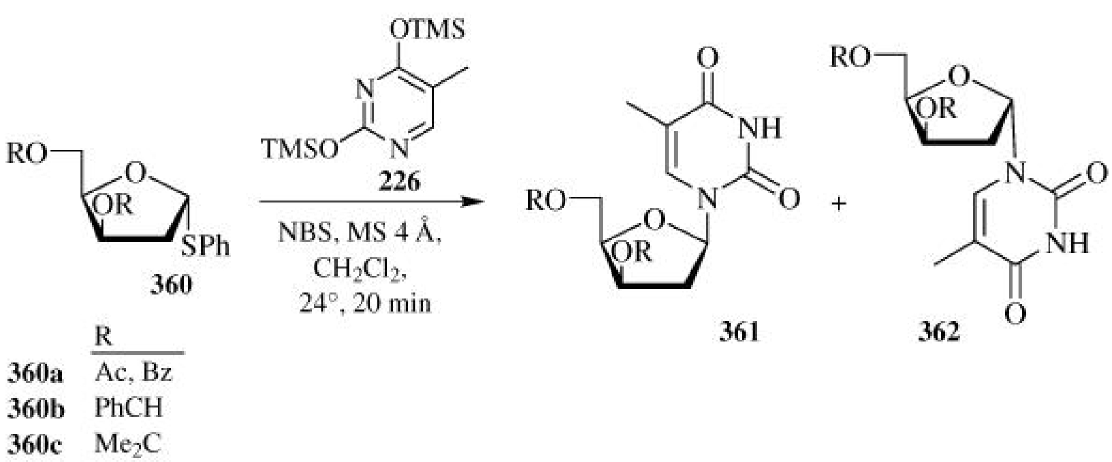


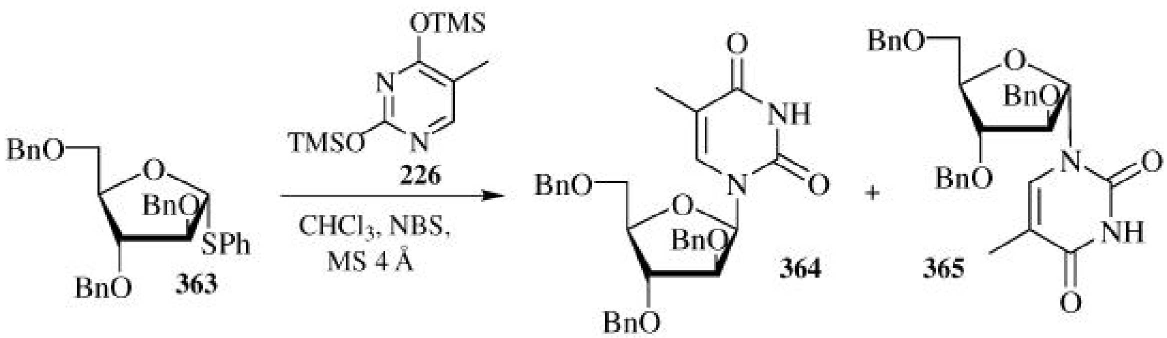
1- α -Phenylthiofuranoside **358a** reacts with silylated thymine **226** via **359** in 70–98% overall yield to form predominantly the α -nucleoside **272**, whereas with the 5-*tert*-butyldimethylsilyloxy derivative **358b** an α / β ratio of **272**/**271** = 3:1 to 2:1 is obtained. (404) The 2-deoxyxylofuranosyl derivatives **360** afford with **226** a ratio of **361**/**362** = 1:12 – 1:30 from benzylidene **360b** and isopropylidene derivative **360c** in the presence of molecular sieves. In contrast, the 5¢-*O*-acetyl or *O*-benzoyl derivatives **360a** give α / β ratios of 1:1.5–1:2. (404a,405)

For further studies with 1-phenylthio-5-*O*-(*tert*-butyldiphenylsilyl)-2,3-dideoxyribofuranosyl derivatives, see Ref. (406). The D-arabinosyl derivative **363** affords predominantly the β -nucleoside **364** (91%) as well as some α -nucleoside **365** (**364**:**365** = 9:1) with **226** with NBS in $CHCl_3$. (407)

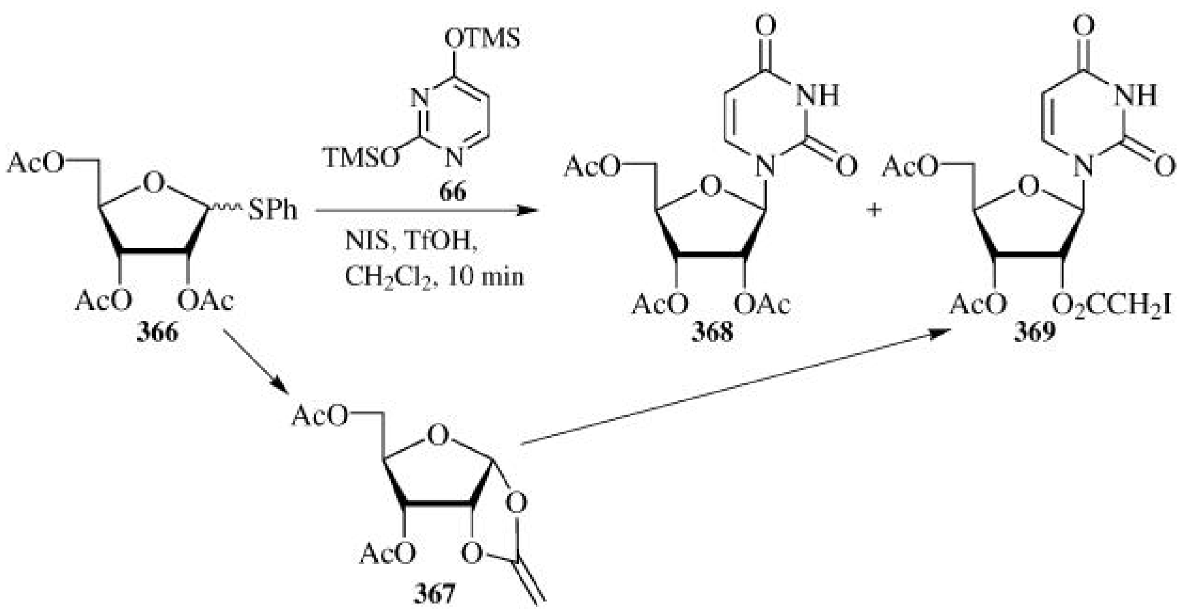
2,3,5-Tri-*O*-acetyl-1-phenylthio-D-ribofuranose (**366**) gives with NIS/ CF_3SO_3H 56% of tri-*O*-acetyluridine (**368**) and, via **367**, 6% of the 2¢-iodoacetyl derivative **369**, whereas silylated N^4-acetyl cytosine **277** affords 81% of



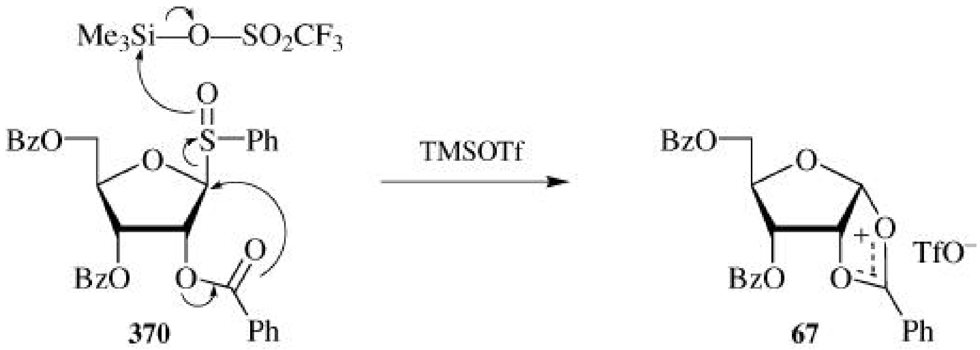




tetraacetylcytidine. (408) For analogous reactions of 1-phenylthio-2,3,4,6-tetra-*O*-acetylglucopyranose with persilylated 2-*N*-acetyl-6-chloropurine, see Refs. 408a, 409.

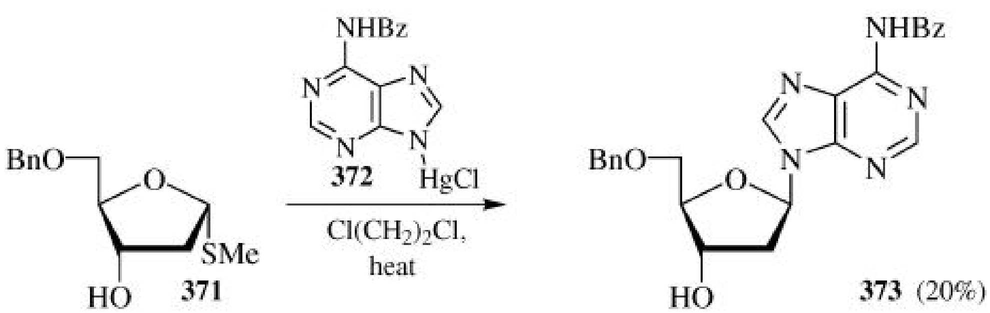


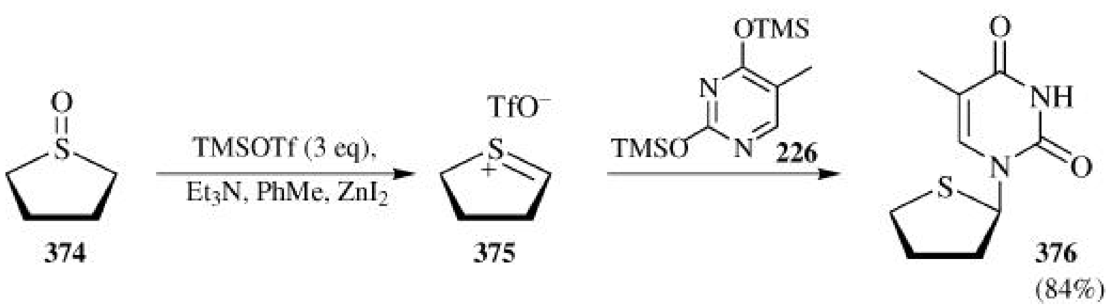
On oxidation of 1-phenylthio derivatives, which are readily available from the protected 1-*O*-methylsugars with thiophenol/$BF_3{\cdot}OEt_2$, (411) with *m*-chloroperbenzoic acid one obtains the corresponding sulfoxides such as **370**. Treatment of these 1-sulfoxides with TMSOTf results in a Pummerer reaction that affords sugar cations such as **67**. Subsequent reaction with silylated bases provides the corresponding protected nucleosides in high yields. (412)



Displacement of the 1 α -methylthio group in **371** by the 9-chloromercuric salt **372** of *N*[6]-benzoyladenine affords via an S_N2 reaction the 5¢-*O*-benzyl ether of 2¢-deoxy-*N*-benzoyladenosine **373** in 20% yield, as well as 28% of the corresponding α anomer. (413)

The related Pummerer reaction of tetramethylene sulfoxide **374** with TMSOTf generates the electrophilic cation **375**, which reacts readily with silylated thymine **226** generated in sit u from thymine to give the tetrahydrothiophene nucleoside **376**

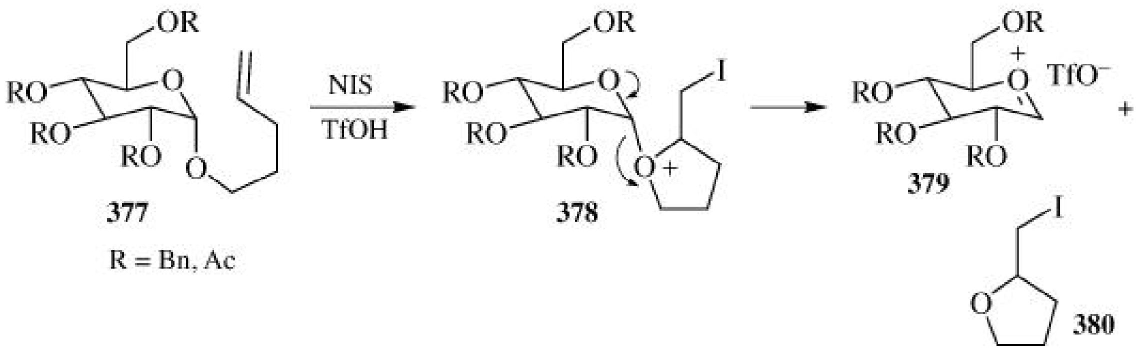




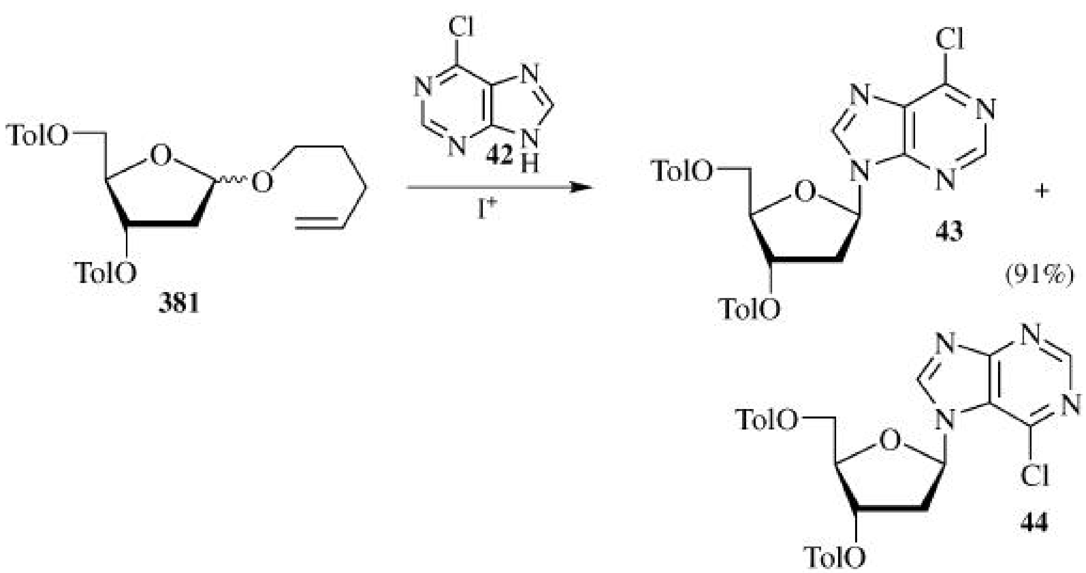
in 84% yield. (414) For other recent Pummerer reactions, see Ref. 414a-414l, and for reviews on 4′-thionucleosides, see Ref. 414m, n.

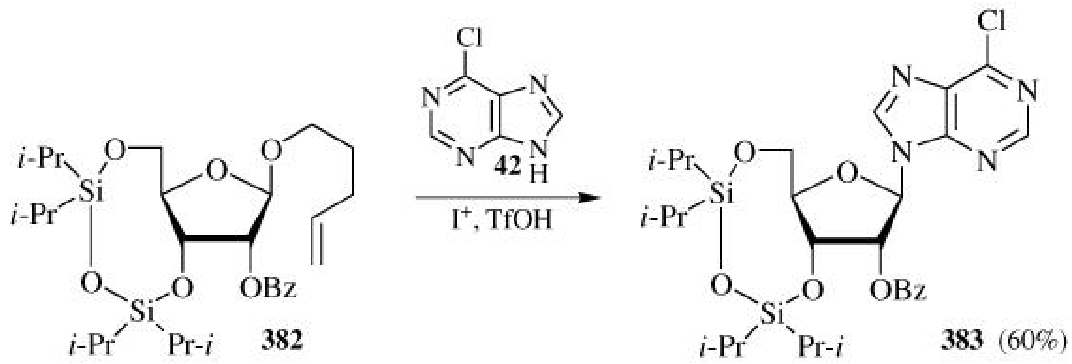
7.1.3. Alternative Formation of 1-Sugar Cations

It was previously emphasized that any method that yields 1-sugar cations as intermediates is potentially useful for the synthesis of nucleosides or glycosides (and vice versa). Thus 4-pentenylgly-cosides **377** are converted by soft electrophiles such as NIS, IDCP, or NBS (415-419) in combination with a Lewis acid such as CF_3SO_3H or $Et_3SiOSO_2CF_3$ via **378** to the reactive sugar cations **379** and 2-iodomethyltetrahydrofuran **380**. In acetonitrile products of a Ritter reaction (199-204) between **379** and acetonitrile can be observed. (420)

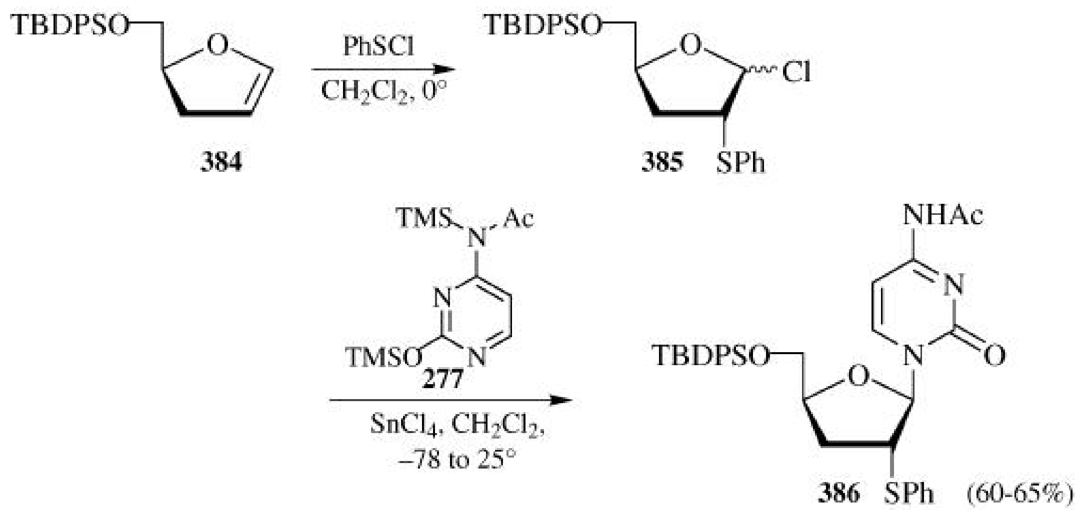


Reaction of glycoside **381** with 6-chloropurine (**42**) and iodonium reagents affords (apparently kinetically controlled) a 91% yield of the N^9- and N^7-nucleosides **43** and **44** as well as the corresponding α anomers, whereas **382** furnishes only **383** in 60% yield. (421)



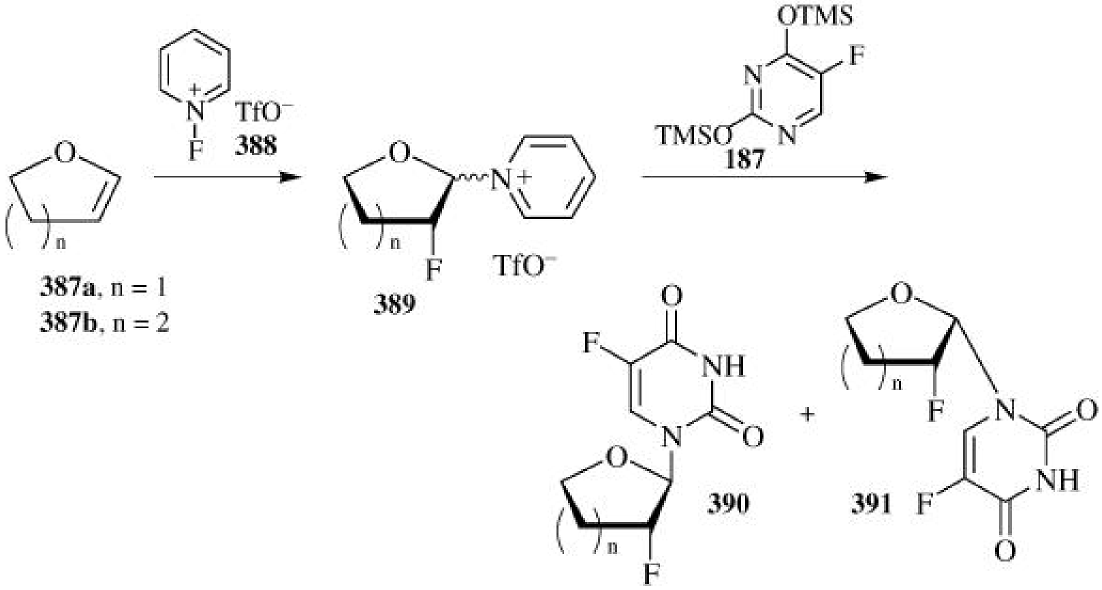


Transformation of the substituted dihydrofuran **384** with phenylsulfenyl chloride gives intermediate **385**, which affords with **277** in the presence of $SnCl_4$ or TMSOTf predominantly the β -nucleoside **386** in 60–65% yield. Since the soft sulfur in **385** complexes better with $SnCl_4$ than with the hard TMSOTf, $SnCl_4$ gives a β / α ratio of 18:1, whereas TMSOTf leads to a β / α ratio of only 6:1. (421a,b)

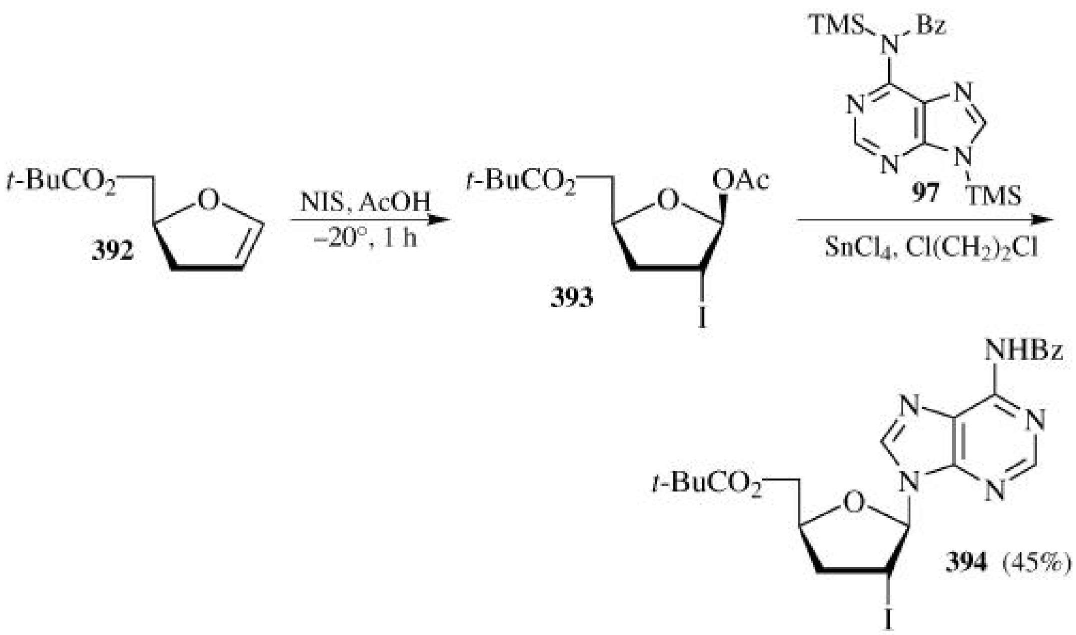


For analogous reactions with phenylselenyl chloride or *N*-iodosuccinimide, see Refs. 421c and 422.

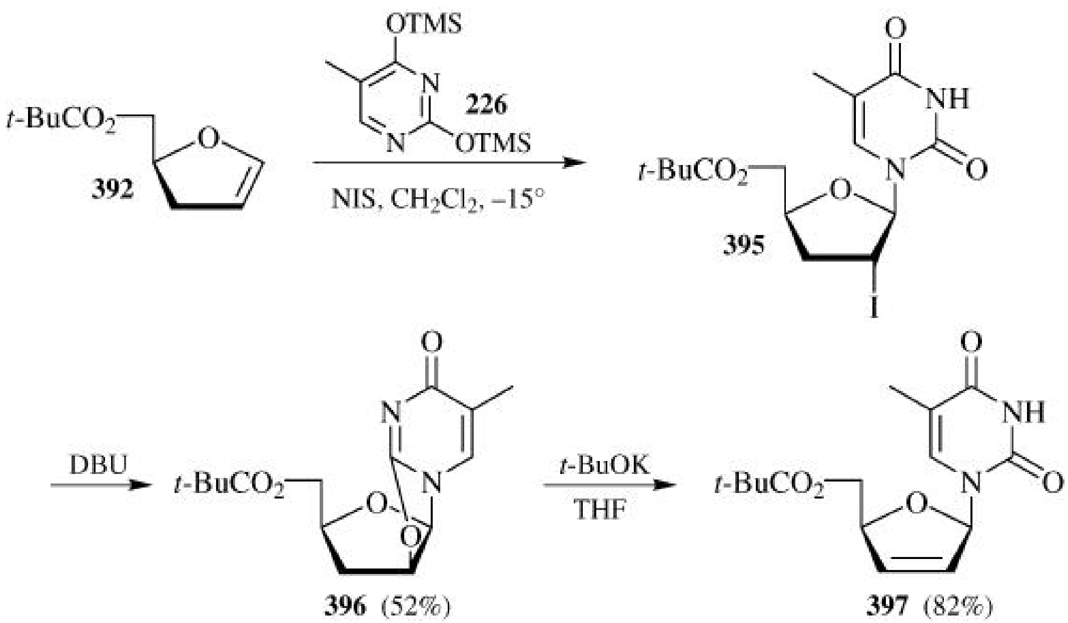
Reaction of dihydrofuran **387a** or dihydropyran **387b** with *N*-fluoropyridinium triflate (**388**) in CH_2Cl_2 produces 2-fluoro-1-pyridinium triflates **389**, which react with silylated 5-fluorouracil **187** in DMF at 120° to give a 3:2 mixture of **390** and **391** in 50–60% yield. (422)



Iodination of dihydrofuran **392** with NIS in acetic acid produces a 14:1 mixture of iodoacetate **393** and its 1,2-epimer, which are reacted without purification with silylated N^6-benzoyladenine (**97**) in the presence of $SnCl_4$ to give the adenosine analog **394** in 45% overall yield. (423) Analogous iodination of **392** in the presence of silylated thymine **226** in CH_2Cl_2 furnishes the thymidine analog **395**.



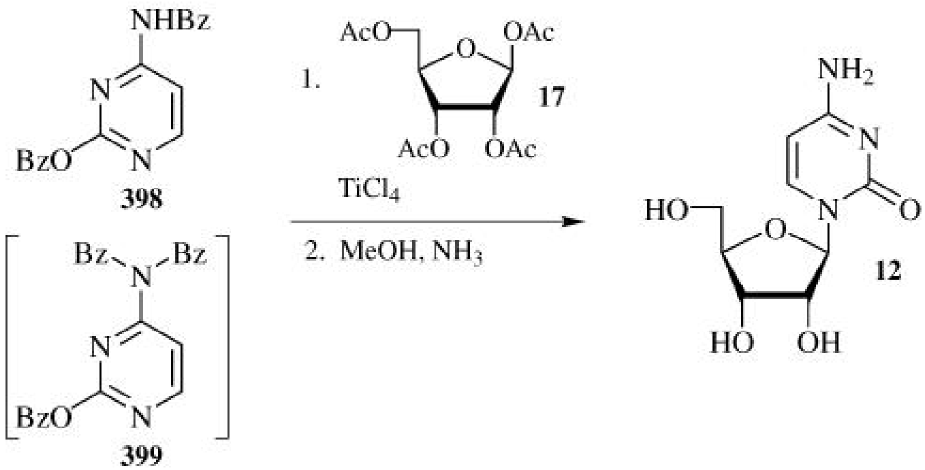
Treatment of **395** with DBU affords the corresponding 2,2¢-anhydronucleoside **396** (52%), which is transformed by potassium *tert*-butoxide in 82% yield into 2¢,3¢-didehydronucleoside **397**. (423) For analogous reactions of **392** with PhSeCl, see Ref. 423a, b.



7.1.4. Variations of the Hilbert-Johnson Reaction

A patent claims the superiority of *N,O*-acylated cytosines compared to the corresponding silylated cytosines, since the *N,O*-acylated cytosines are not moisture labile. (424)

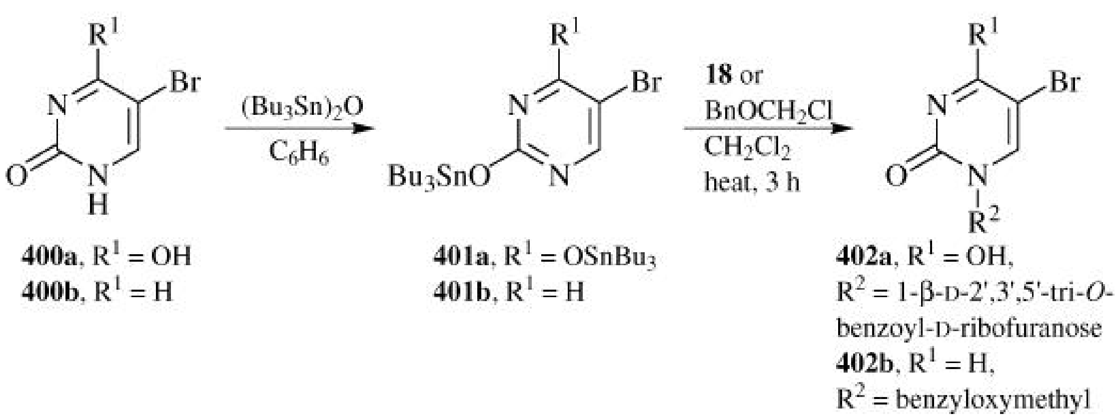
On acylation of cytosine with benzoyl chloride/triethylamine in 1,2-dichloroethane, cooling to 10° and filtering the precipitated triethylamine hydrochloride, the filtrate contains 2,4-di-*O,N*-benzoy lcytosine (**398**) or 2,4,4-tri-*O,N*-benzoyl cytosine (**399**), both of which can be isolated in crystalline form or reacted as a



mixture in situ with **17** in the presence of $TiCl_4$, TMSOTf, or $SnCl_4$ to give on workup and saponification free cytidine in up to 90% yield. (424) Other publications describe, however, that during benzoylation of pyrimidine bases with benzoyl chloride-pyridine, the N^1,N^3-dibenzoylpyrimidines are obtained predominantly. (425,425a–c)

One should realize, however, that in nucleoside synthesis the cost of the silylation of the heterocycles is minute compared to the preparation of the sugar synthons or special heterocyclic bases.

Heating of **400a** and **400b** with bis(tributyltin)oxide in benzene with removal of water gives 2,4-bis(tributylstannyloxy)-5-bromopyrimidine (**401a**) or 2-tributylstannyloxy-5-bromopyrimidine (**401b**), which react readily with the standard sugar **18** in the presence of $SnCl_4$ or with reactive α -haloethers such as benzyloxymethyl chloride under mild conditions to afford 85–97% of the corresponding nucleoside **402a** (426) or the nucleoside analog **402b**. (427)



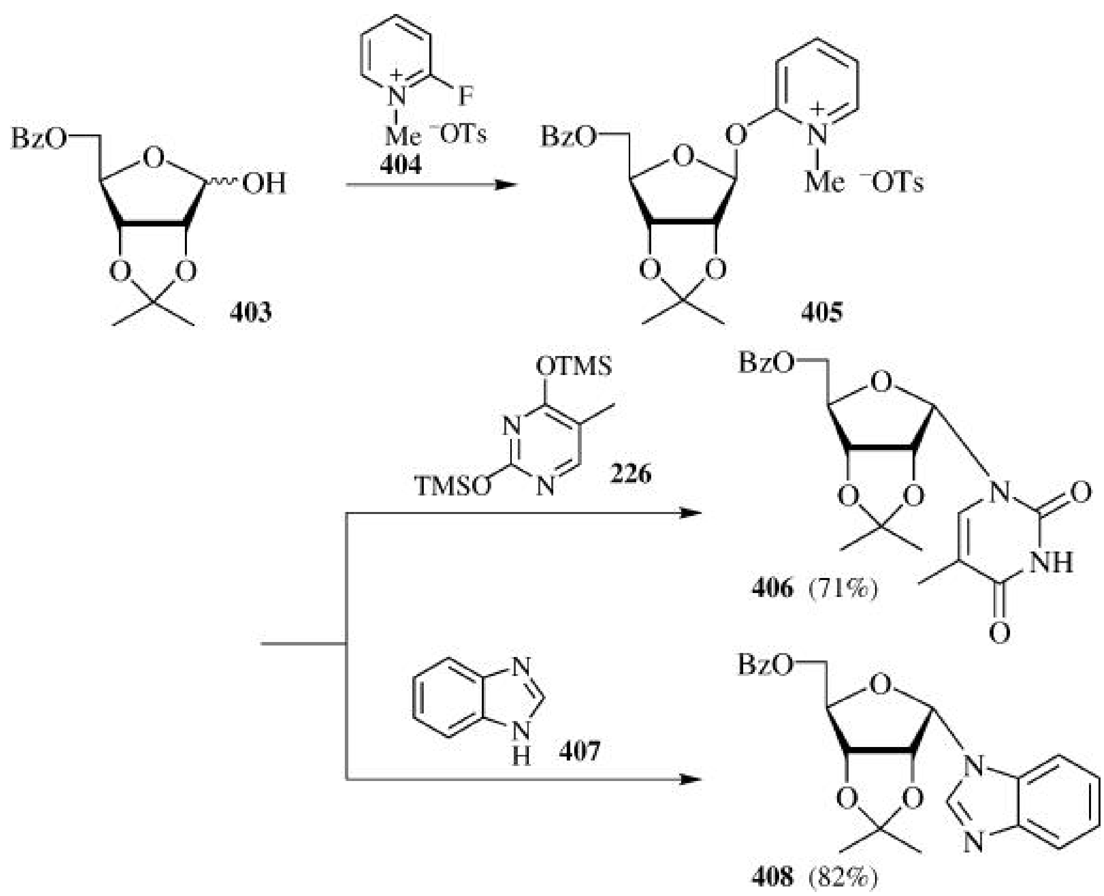
Although these alternatives to the Silyl-Hilbert-Johnson reaction seem to be effective, the enviromental problems connected with the large-scale use of expensive and toxic tin compounds may restrict their use to special cases.

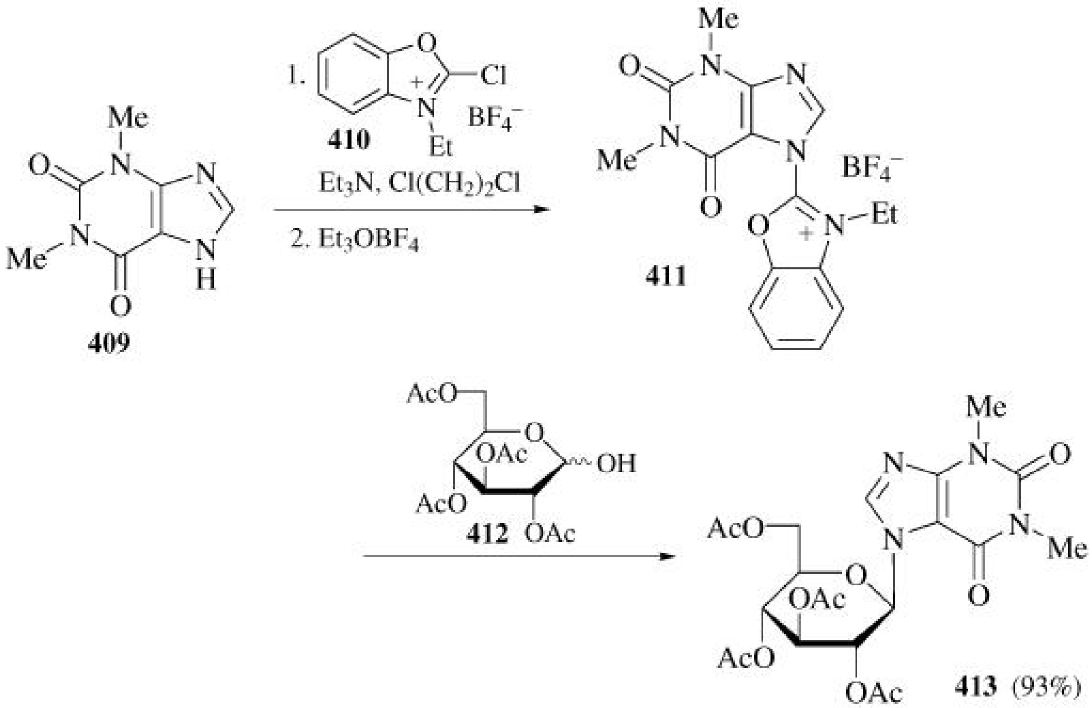
8. Alternative Nucleoside-Forming Reactions

8.1. Nucleoside Synthesis with Protected 1-Hydroxysugars

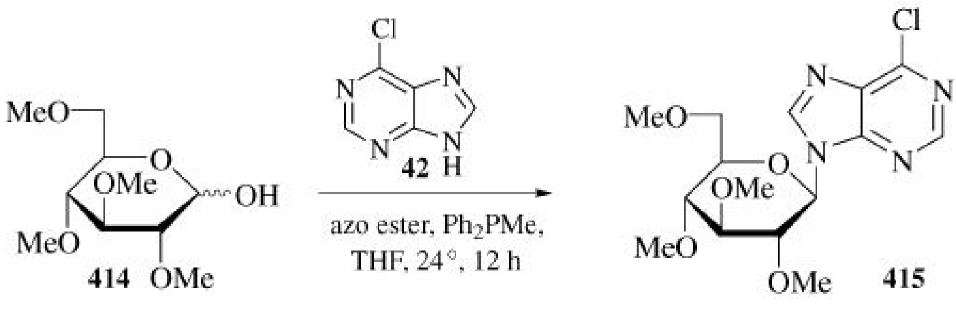
Protected 1-hydroxysugars such as **403** can be activated by *N*-methyl-2-fluoropyridinium tosylate **(404)** to **405**, which reacts with silylated heterocycles such as silylated thymine **226** or 5,6-benzimidazole **(407)** to give primarily the α -nucleosides (α / β = 98:2-8:2) **406** and **408** in 71 and 82% yield, respectively. (428) Activation of theobromine **(409)** with **410** followed by reaction with triethyloxonium tetrafluoroborate gives **411**, which on addition of **412** affords N^7-nucleoside **413** in 93% yield. (429)

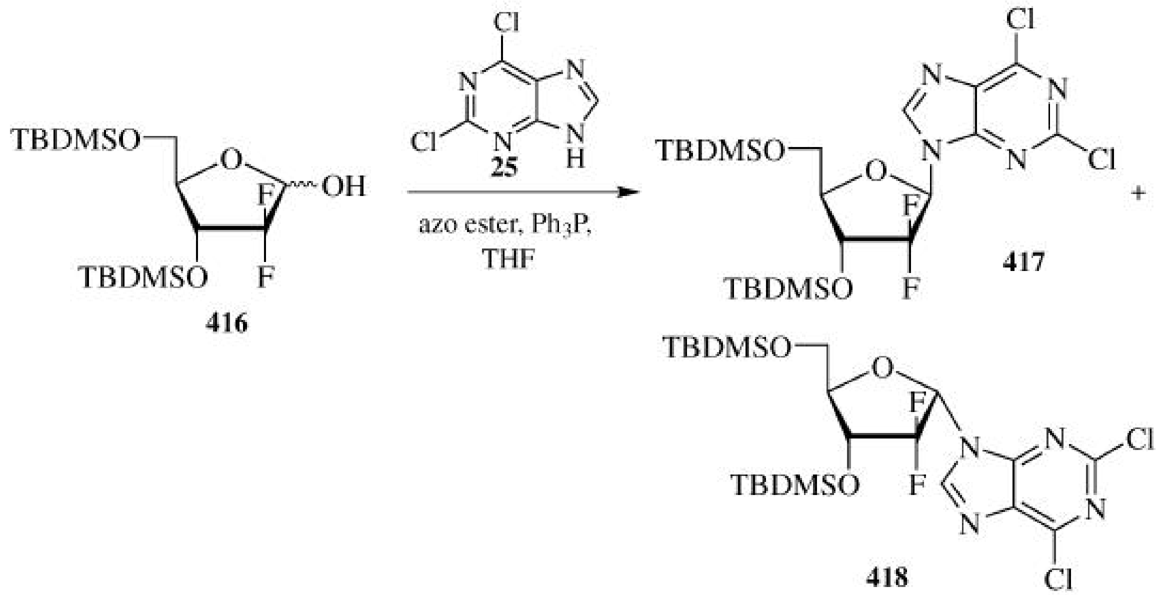
Activation of protected 1-hydroxysugars under Mitsunobu conditions permits the reaction of glucopyranose **414** with **42** to give nucleoside **415** in 66% yield, (430) whereas Mitsunobu coupling of difluororibose **416** with **25** affords 50% of a 1:1 anomeric mixture of **417** and **418**. (431) The 1-*O*-mesylate **276**, however, reacts smoothly with silylated cytosine in the presence of TMSOTf to give 2 -deoxy-2 ,2 -difluorocytidines **278** and **279** in high yield (Eq .**97**, p. 57). Likewise, the

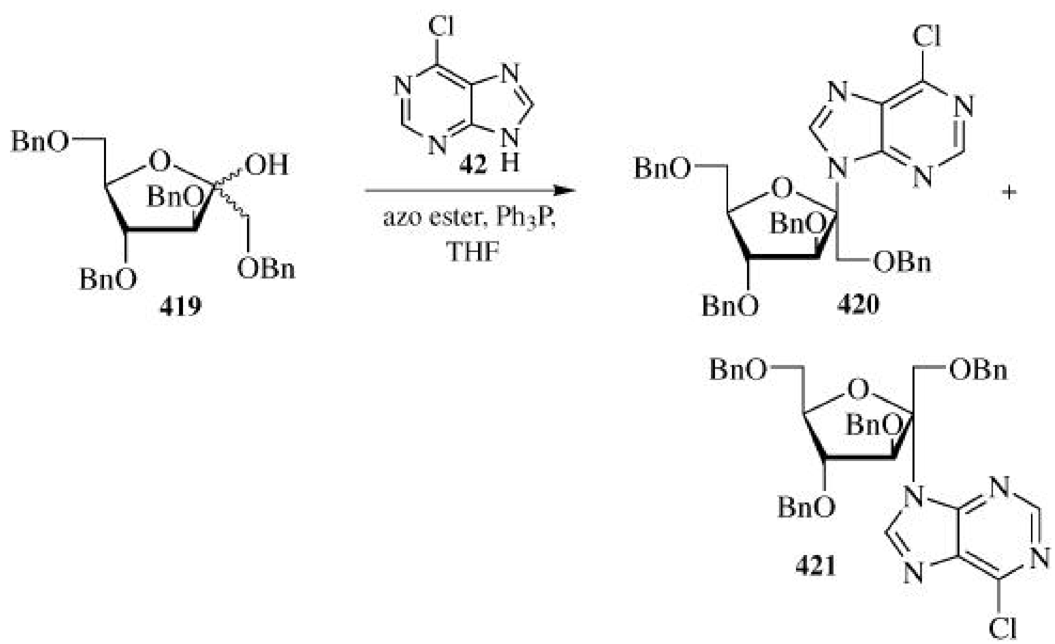




fructose derivative **419** analogously furnishes with **42** an α / β anomeric mixture of nucleosides **420** and **421** in 32% yield. (432) For recent applications of the Mitsunobu reaction, see Refs. 432a–h.

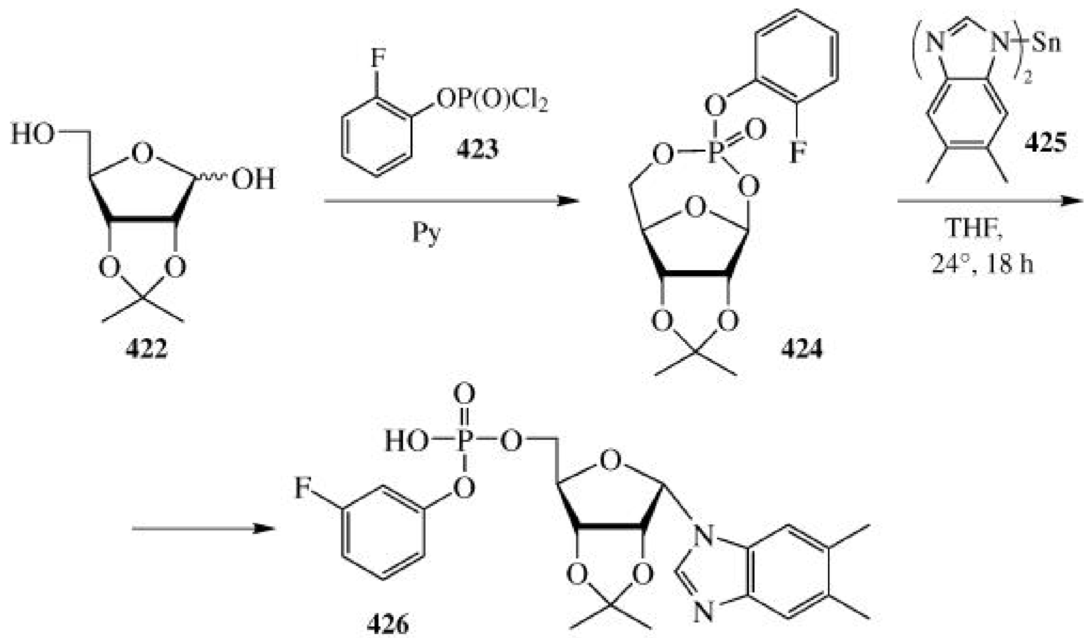




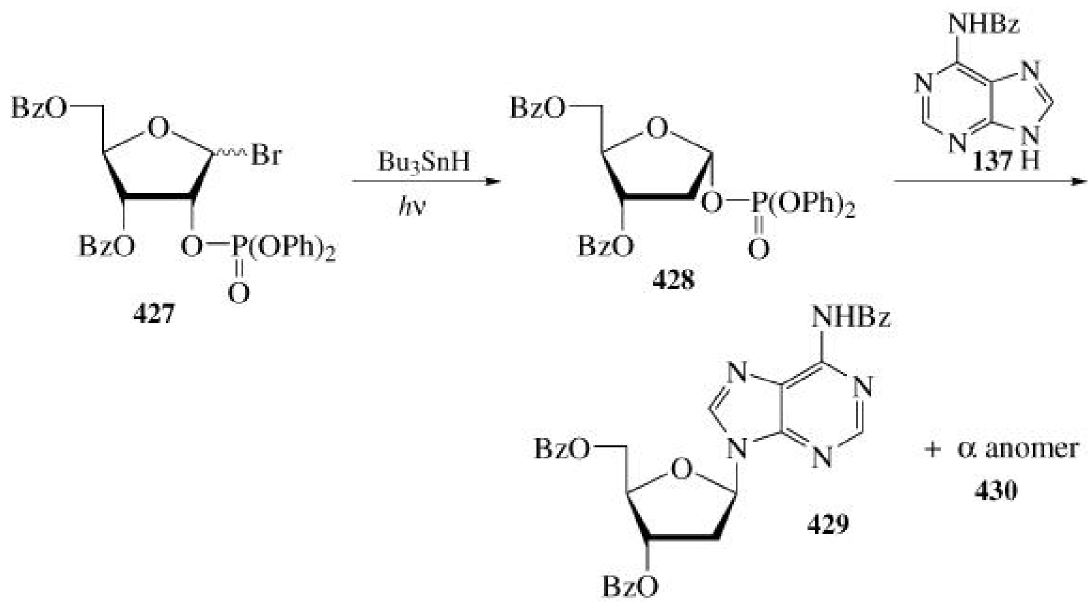


Related to the Mitsunobu reaction, which gives rise to activated 1-*O*-triphenylphosphonium intermediates, reaction of 2,3-*O*-isopropylidene-D-ribofuranose **422** with 2-fluorophenyl phosphorodichloridate **423** affords the activated cyclic 1,5-arylphosphate intermediate **424**. Reaction of **424** with Sn(II) derivatives of heterocyclic bases such as 5,6-dimethylbenzimidazole **425** furnishes the α -nucleoside **426** in

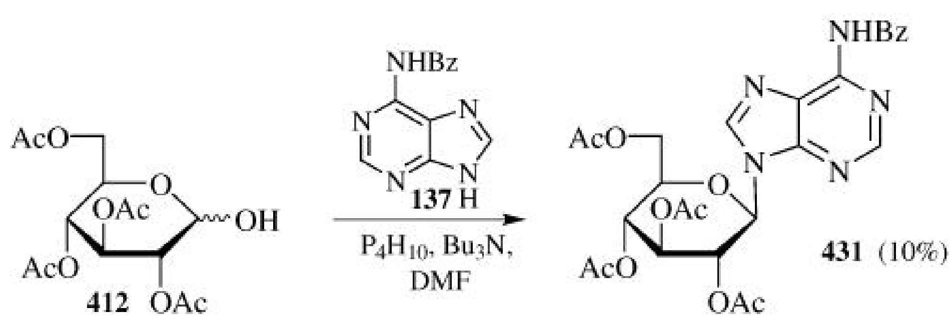
81% yield, whereas the analogous derivative of 6-(1-piperidino)purine affords only 30% of the corresponding α -purine nucleoside. Tin derivatives such as **425** are prepared by treatment of the heterocyclic bases with butyllithium followed by $SnBr_2$. (433)



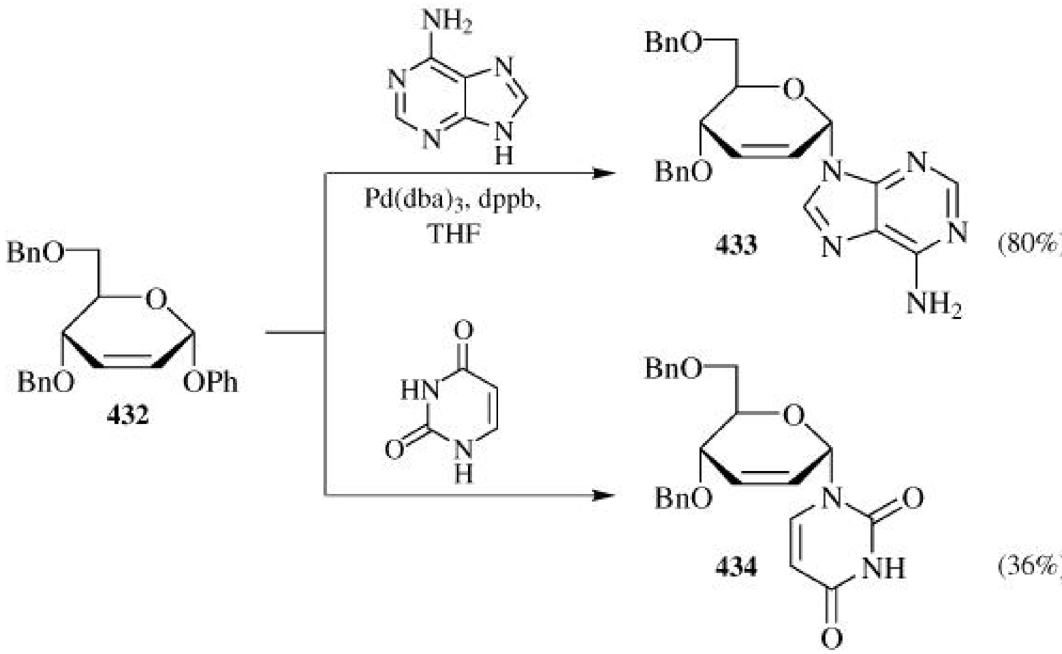
Radical rearrangement of 3,5-di-*O*-benzoyl-2-*O*-(diphenylphosphoryl)-D-ribofuranosyl bromide (**427**) with tributyltin hydride affords the sensitive activated α -D-ribofuranose **428**, which reacts with N^6-benzoyladenine to give 42% of a 1:1 mixture of the anomeric nucleosides **429** and **430**. (434)



Following the pioneering studies by E. Fischer (435) in 1909 on the activation of 1-hydroxysugars with P_4O_{10}, G. Schramm (436) and other investigators (437-439) studied the reactions of protected 1-hydroxysugars with P_4O_{10} in DMF or $CHCl_3$. Thus D-glucopyranose **412** condenses with N^6-benzoyladenine (**137**) with P_4O_{10} in DMF to give after ion-exchange chromatography 9- β -D-glucopyranosyladenine (**431**) in 10% yield. (437) Condensations of purines with 2-deoxy-D-ribose in the presence of P_4O_{10}/Bu_3N give rise to 2,3-dideoxy-3-purine-substituted *C*-nucleosides. (438, 439)

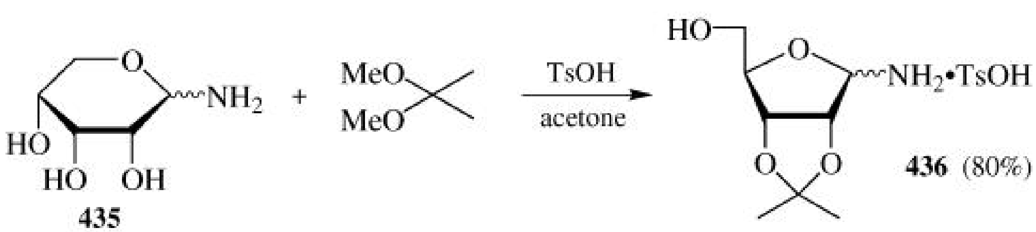


Reaction of Ferrier intermediate **432** with adenine or uracil in the presence of $Pd(dba)_3$ and bis-1,4-(diphenylphosphino)butane (dppb) in THF furnishes α -nucleosides **433** and **434** in 80% and 36% yield, respectively. (440) For analogous reactions with furanoses, cf Ref. (440a).

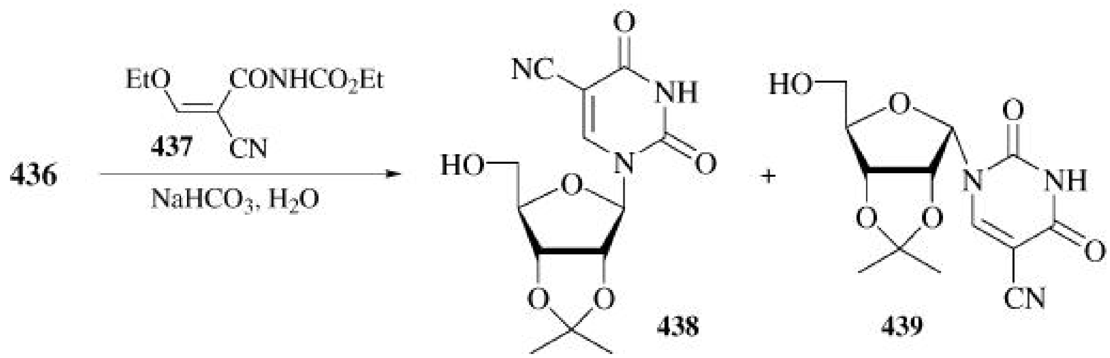


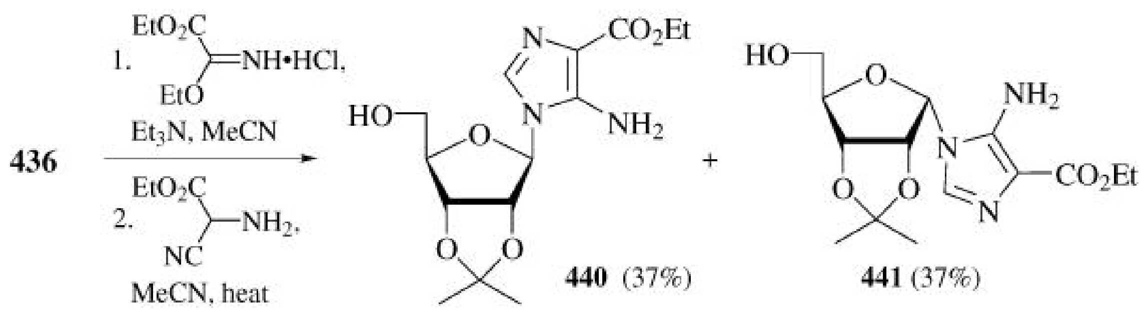
8.2. Construction of the Heterocyclic Base to Unsaturated Systems

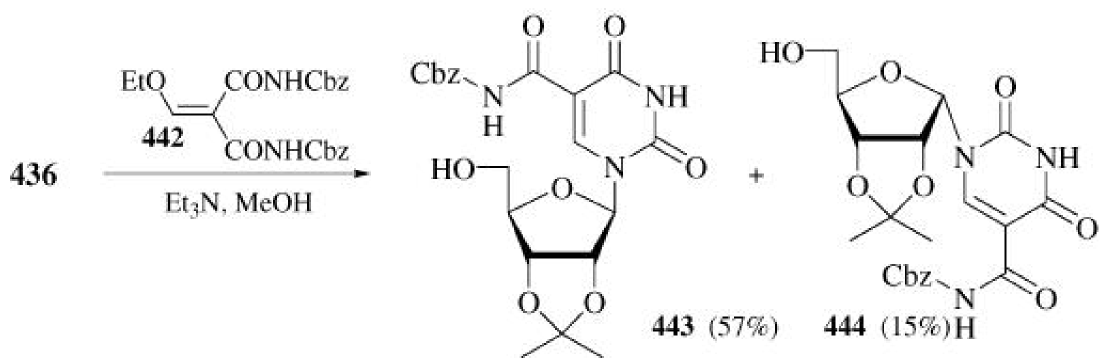
Treatment of D-ribose with methanolic ammonia gives 90% of D-ribopyranosylamine **435**, which is converted by 2,2-dimethoxypropane, acetone, and *p*-toluenesulfonic acid into the crystalline D-ribofuranosylamine tosylate **436** in 80% yield. (441) Reaction of **436** with ethyl *N*-(α -cyano- β -ethoxyacryloyl)carbamate



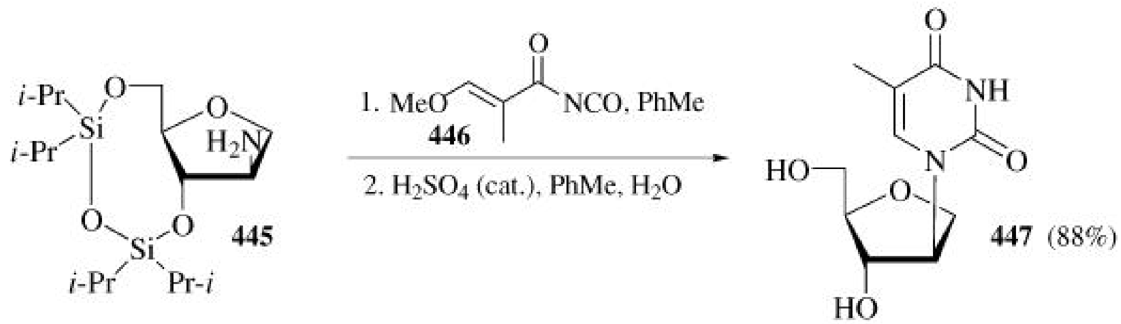
437 furnishes an anomeric mixture of 8% of the β anomer **438** and 15% of the α anomer **439**. Analogous reaction of **436** with ethyl formimidate hydrochloride followed by heating with ethyl α -amino- α-cyanoacetate affords 37% of the β anomer **440** as well as the α anomer **441**. (441) For an analogous reaction of 1-amino-2-deoxy-2- α -fluoro-3,5-di-*O*-benzoylribose with a derivative of ethyl 2-aminocyanoacetate, see Ref. 442.

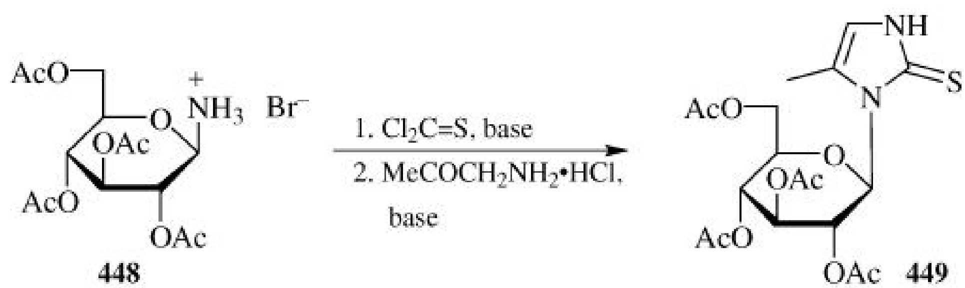




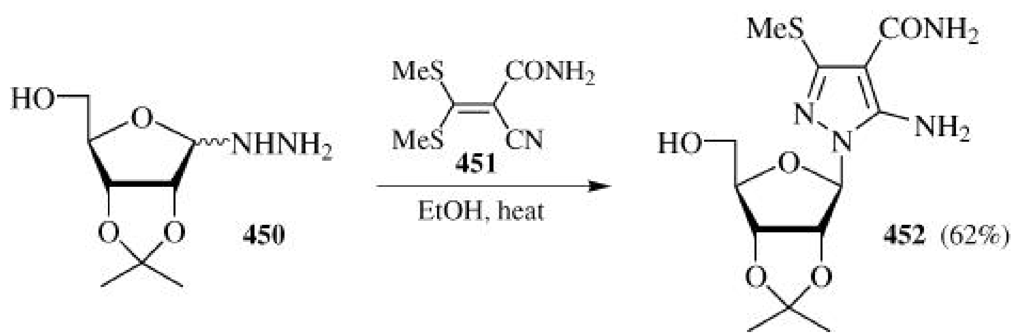


Condensation of **436** with *N*,*N* -(benzyloxycarbonyl)ethoxymethylenemalonamide (**442**) furnishes 57% of the β anomer **443** and 15% of the α anomer **444**. (443) On using 3-methoxy-2-methacryloyl isocyanate (**446**), **445** is converted into the thymidine analog **447** in 88% yield. (444) See also the reaction of protected 1-isocyanatosugars. (445)

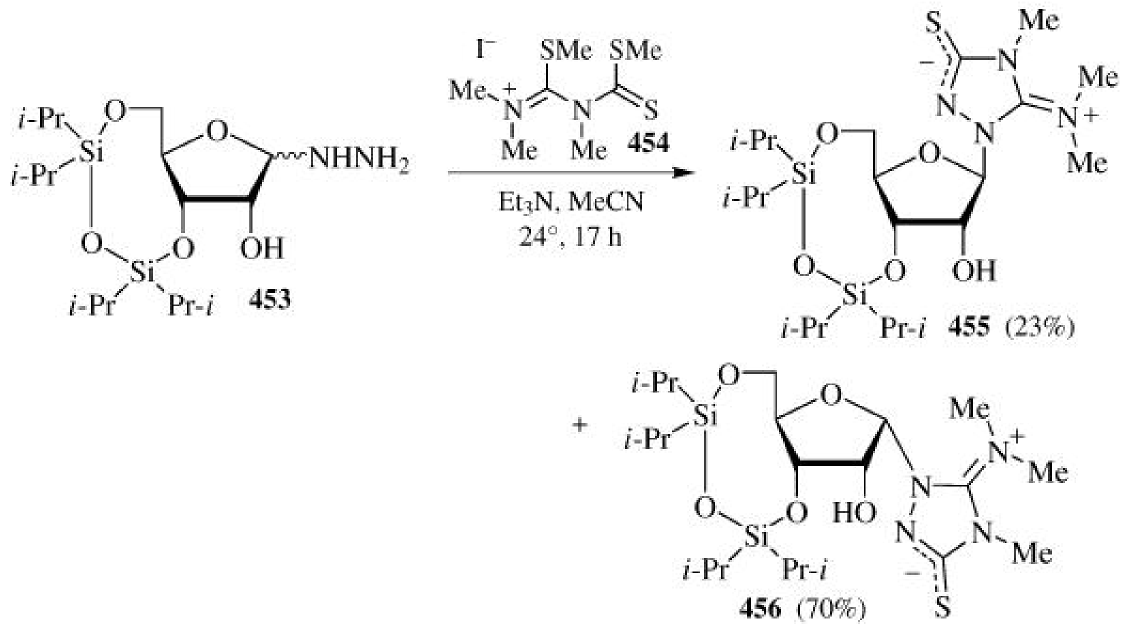


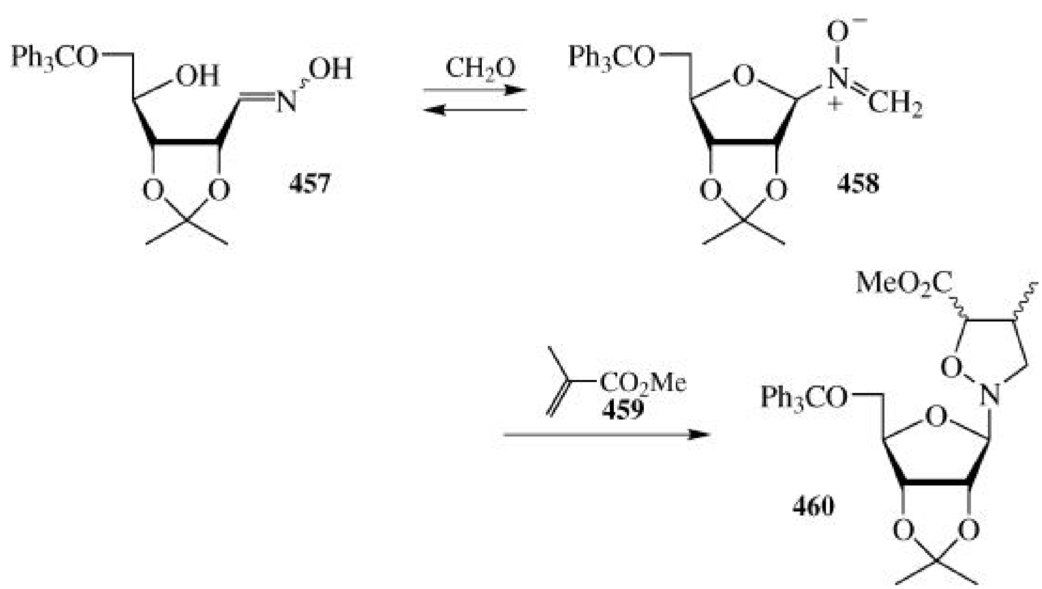


Treatment of β -D-glucopyranosylamine hydrobromide **448** with thiophosgene affords an intermediate 1-isothiocyanate, which condenses with aminoacetone hydrochloride to the nucleoside **449**. (446) Reaction of D-ribofuranosylhydrazine **450** with ketenethioacetal **451** furnishes the pyrazole nucleoside **452** in 62% yield, (447, 448) whereas the protected hydrazine derivative **453** gives with thiouronium salt **454** 23% of mesoionic β anomer **455** and 7% of α anomer **456**. (449) For analogous cycloadditions of protected 1-azidosugars, see Ref. 450.



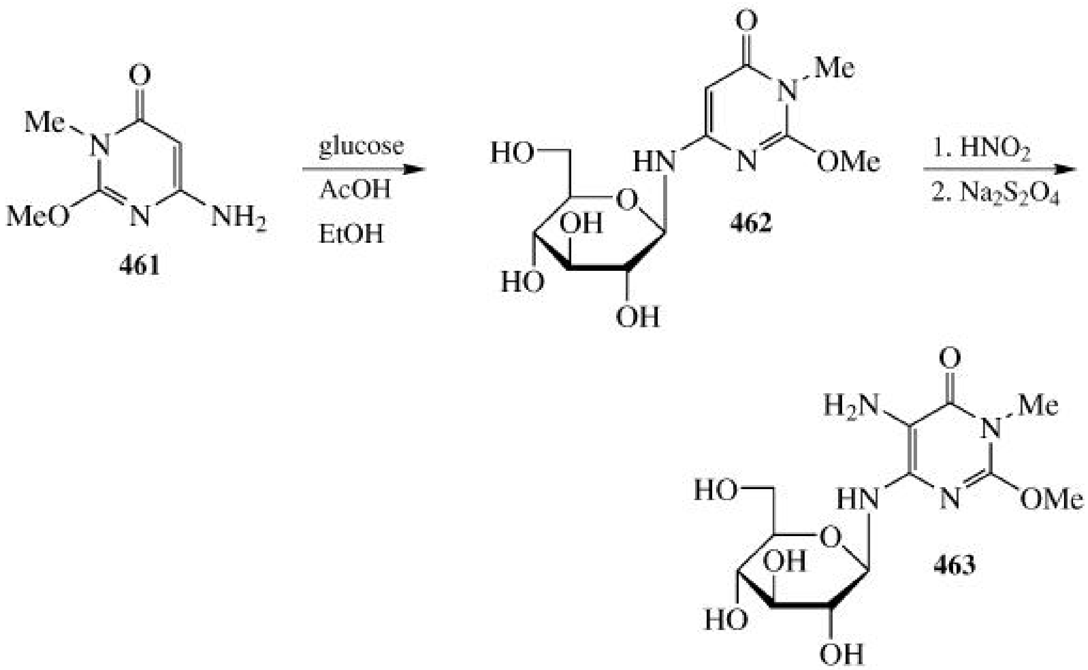
The easily accessible protected *E/Z* mixture of 1-oximes **457** reacts with formaldehyde and methyl methacrylate (**459**) to give via **458** a mixture of the stereoisomers **460** in good yield. (451, 452)

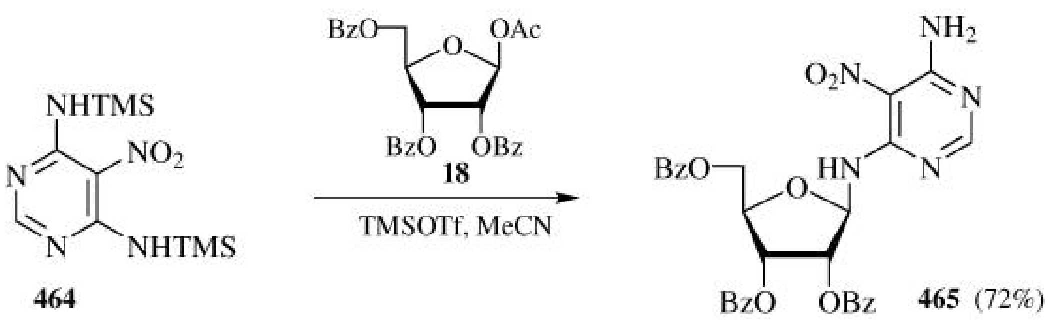




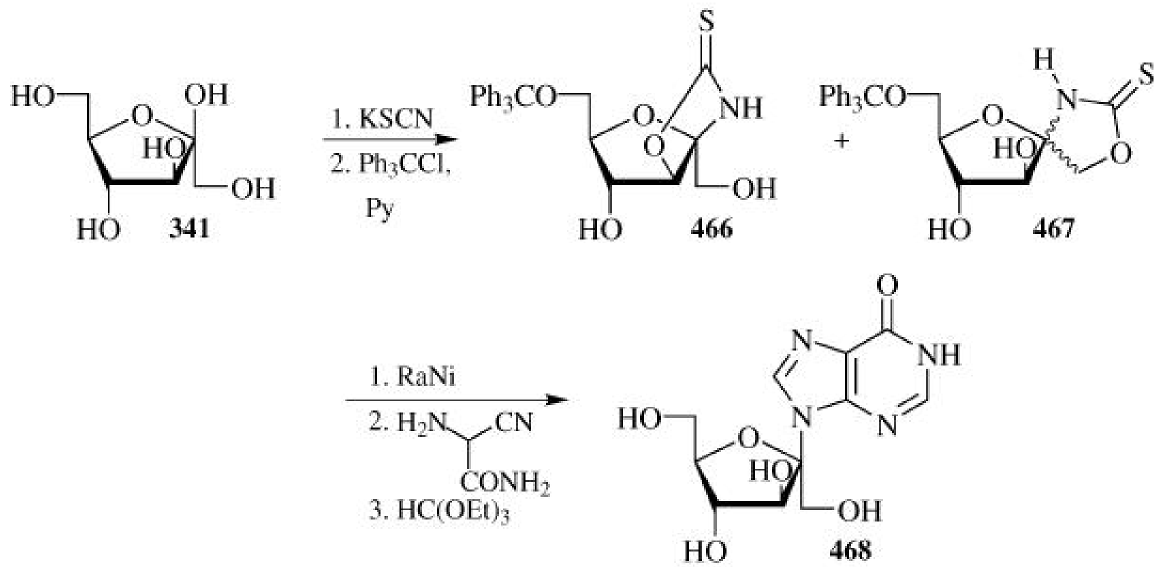
The condensation of the 6-aminopyrimidin-4-one **461** with glucose to yield **462** followed by nitrosation and reduction affords intermediate **463**, (453, 454) which is converted by formamidine acetate (454) to the corresponding purine nucleoside or with nitrous acid to the corresponding 8-azapurine nucleoside. It should be emphasized, however, that silylated amino heterocycles such as **464** react with ribose derivative **18** in the presence of TMSOTf in acetonitrile to give adenosine precursor **465** in 72% yield. (455)

Furthermore, D-fructose (**341**) condenses with KSCN in aqueous HCl followed by treatment with triphenylmethyl chloride in pyridine to afford a 1:1 mixture of **466** and **467** in high yield. Desulfurization of the mixture of **466** and **467** with Raney Nickel and subsequent reaction with α -amino- α -cyanoacetamide followed



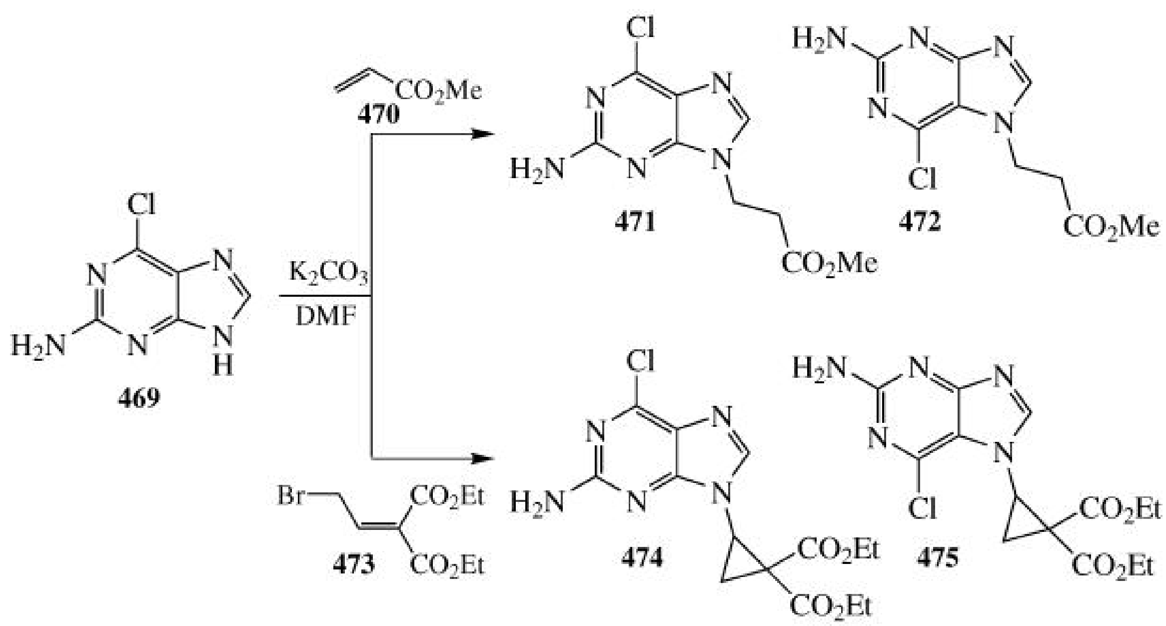


by triethyl orthoformate/acetic anhydride gives a good yield of hypoxanthine nucleoside **468**. (455a)



8.3. Conjugate Additions of Heterocyclic Bases to Unsaturated Systems

Two recent examples of such conjugate additions may suffice. Purines **469** react with methyl acrylate in the presence of K_2CO_3 in DMF to give the corresponding N^9-Michael adduct **471** and small amounts of the N^7-adduct **472** in 85% yield. (456) Ethyl 2-bromoethylenemalonate (**473**) affords the substituted cyclopropanes **474** and **475** in an 8:1 ratio in 87% yield. (456) For additional examples, see Refs. 457–460,460a.

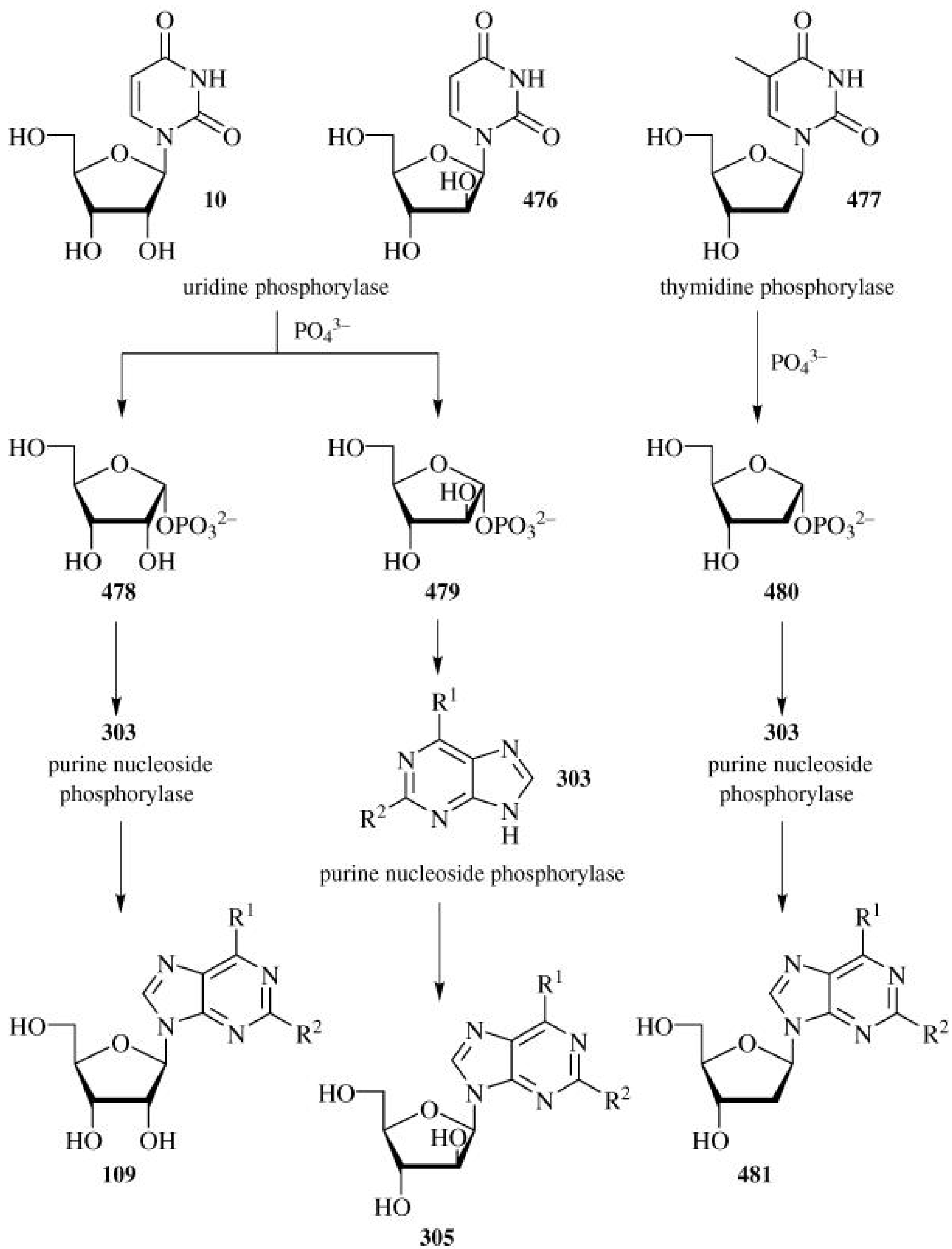


8.4. Enzymatic Transglycosylations

Uridine phosphorylase (EC 2.4.2.3) or thymidine phosphorylase (EC 2.4.2.4) degrades uridine, 1- β -D-arabinofuranosyluracil (ara-U) (**476**) as well as thymidine (**477**) in the presence of phosphate to the corresponding pentose-1-phosphates **478, 479** and **480**, which are transformed in situ by added purines **303** and purine nucleoside phosphorylase (EC 2.4.2.1) to the corresponding purine nucleosides **109**, **305**, and **481**. The application of all these methods in the synthesis of antiviral agents has been reviewed recently. (461)

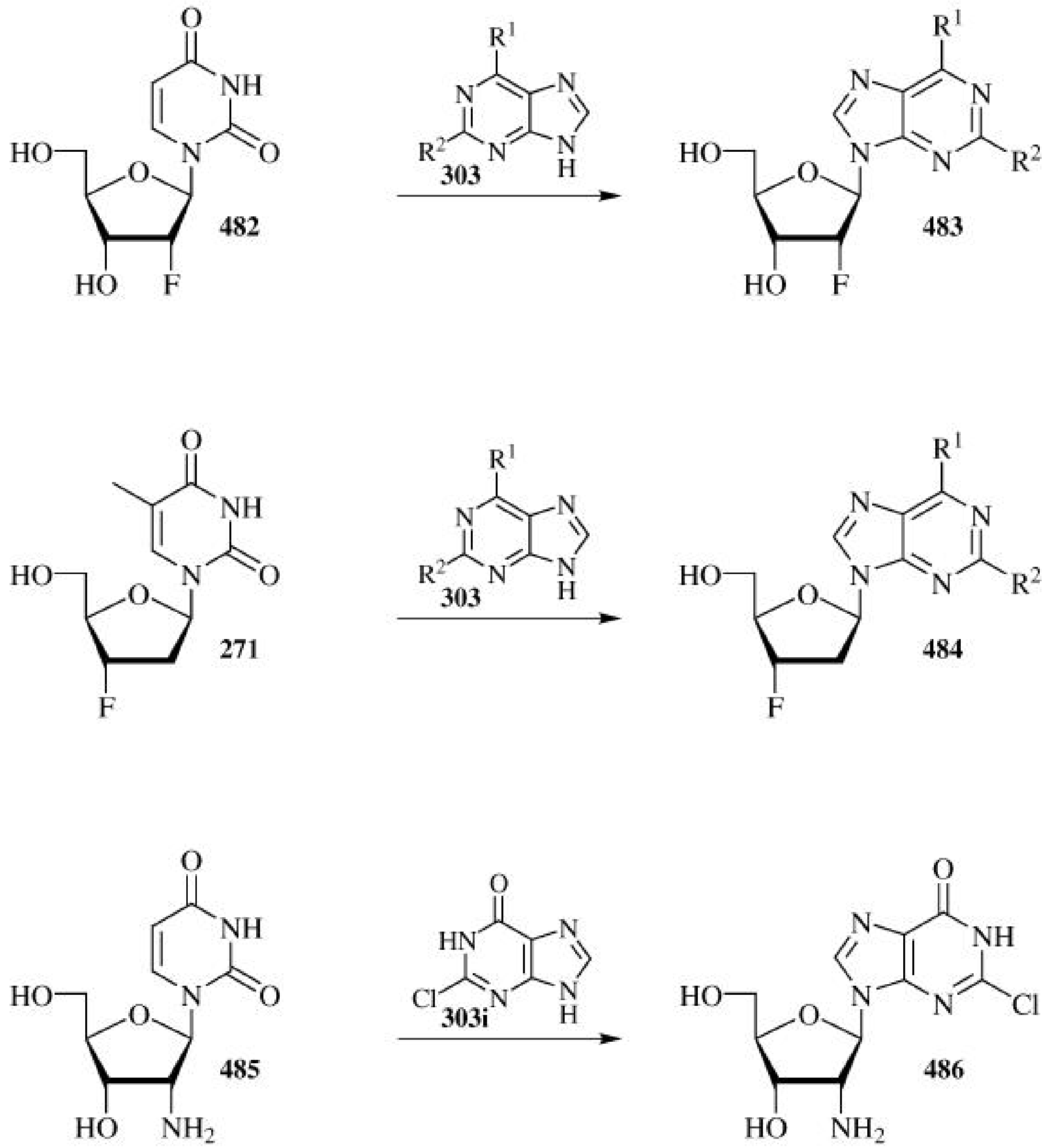
Whereas normal purine nucleosides can be readily synthesized with $SnCl_4$ or TMSOTf as catalyst, enzymatic methodology also permits the synthesis of imidazo[4,5-*c*]pyridine nucleosides (i.e., 3-deazapurine nucleosides). (462) Of particular interest is the transglycosylation of ara-U **476**, (463-467) which is readily available from uridine via 2,2′-anhydrouridine, to give arapurine nucleosides **305**, since these nucleosides are accessible in only moderate yields by chemical synthesis. Equally important are the transglycosylations of thymidine **477** with bases such as 6-dimethylaminopurine to give the corresponding 2′-deoxypurine nucleoside **481** ($R^1 = N(CH_3)_2$;R^2 = H) in 81% yield. (468)

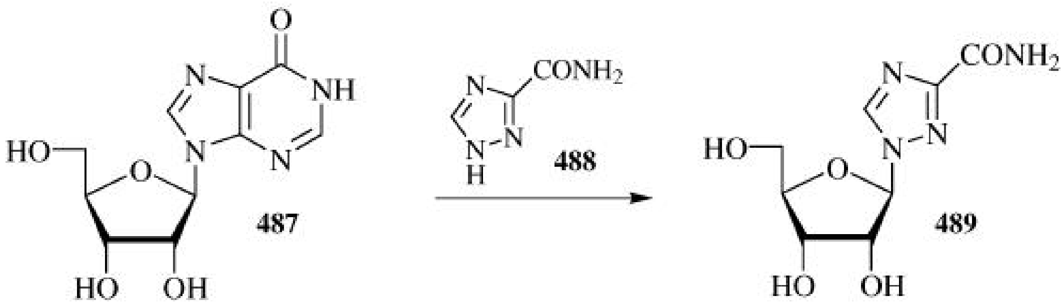
The combination of thymidine phosphorylase and purine nucleoside phosphorylase from *E. coli* (468, 469) can also be used to transform 2′-deoxy-2′-fluorouridine (470-472) (**482**) or 2′,3′-deoxy-3′-fluorothymidine (**271b**) (473) with purines **303** to the corresponding purine nucleosides **483** and **484**.



Enzyme preparations from *Erwinia herbicola* permit the similar transformation of 2′-deoxy-2′-aminouridine (**485**) with 2-chlorohypoxanthine to **486** in 32% yield. (474, 475)

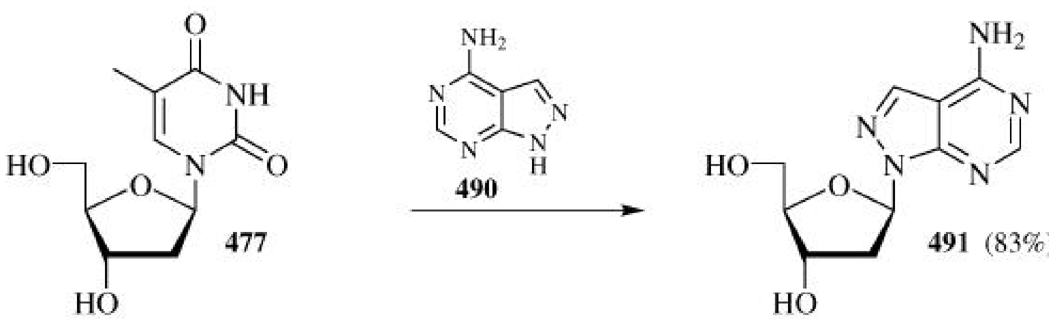
Interestingly, purine nucleosides can also be used as sources of pentose-1-phosphates. Thus inosine (**487**) can be transformed by a purine nucleoside phosphorylase from *Enterobacter aerogenes* (476) in the presence of 1,2,4-triazole-3-carboxamide (**488**) to virazole (**489**). (477)

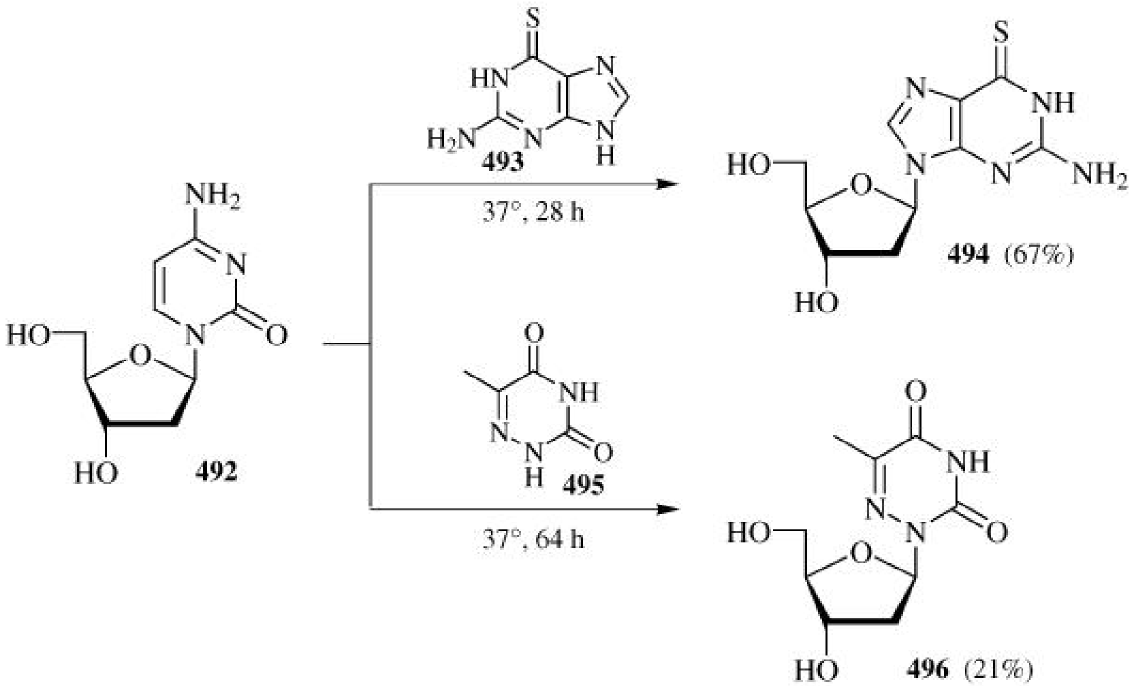




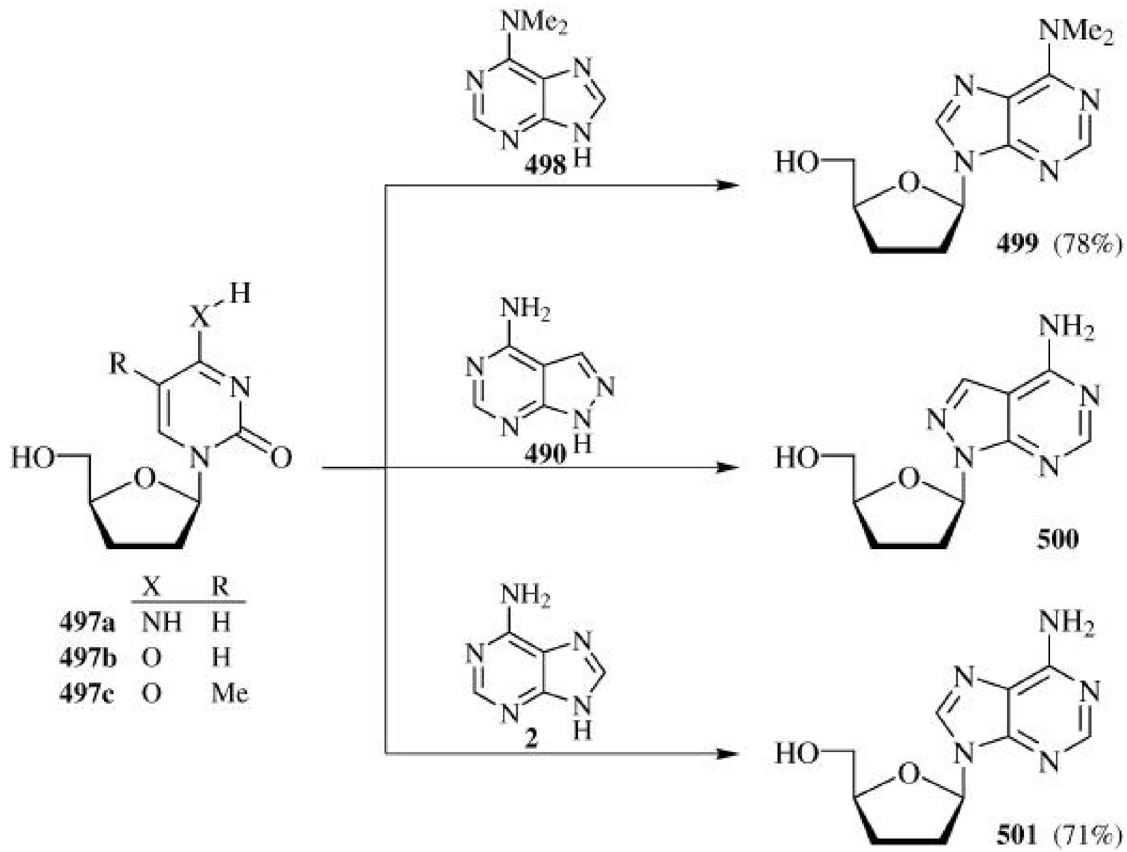
The enzymatic phosphorolysis of purine nucleosides such as inosine (**487**) or guanosine can be made irreversible and thus much more efficient by methylation of the *N*^{7}-nitrogen in **487** or **5** to afford in the presence of 1,2,4-triazole-3-carboxamide (**488**) 44% of virazole (**489**) or with 3-deazaadenine 53% of 3-deazaadenosine. (478)

In earlier studies, the enzyme nucleoside 2 -deoxyribosyltransferase (EC 2.4.2.6) from *Lactobacillus leichmannii* was used to catalyze large-scale transglycosylation reactions of excess thymidine (**477**) with 4-aminopyrazolo[3,4-*d*]-pyrimidine (**490**) to **491** in 83% yield. (479) See also an analogous reaction with 6-dimethylaminopurine. (480) Excess 2 -deoxycytidine (**492**) and 6-thioguanine (**493**) or 6-azathymine (**495**) afford **494** and **496** in 67% and 21% yield, respectively. (479) The same enzyme system permits the preparation of a series of substituted 2 -deoxypurine nucleosides as well as of 1-deazapurine nucleosides. (481, 482) Other bases used for enzymatic transglycosylations are benzimidazole and 5-aminoimidazole-4-carboxamide. (481, 483)





The nucleoside deoxyribosyltransferase II from *Lactobacillus leichmannii* also effects the transfer of the 2′,3′-dideoxyribose moiety from 2′,3′-dideoxycytidine (**497a**) to purine bases such as 6-dimethylaminopurine (**498**) to give **499** in 78% yield (484, 485) and other bases such as 4-aminopyrazolo[3,4-*d*]pyrimidine (**490**) (484) to give **500**, whereas 6-alkoxypurines react with 3′-deoxythymidines in the presence of thymidine and purine phosphorylases to give the corresponding 6-alkoxypurine nucleosides. (486) Further, purine bases such as 1,7-dimethylguanine can also be used. (487) The analogous transglycosylation of 2′,3′-dideoxycytidine **497a**, 2′,3′-dideoxyuridine **497b**, or 2′,3′-dideoxythymidine **497c** with adenine (**2**) to 2 ,3 -dideoxyadenosine **501** in 71% yield can also be catalyzed by transferase enzymes from *E. coli* (488-491) or *Lactobacillus helveticus*. (492) Starting from the easily accessible uracil or cytosine arabinosides **300**, analogous enzymatic transglycosylations with a variety of purines such as **498** or 2-fluoro-6-aminopurine proceed in up to 60% yield. (382-382a)



Although the preparation of these transferase enzymes is quite elaborate, once an enzyme preparation is isolated, it becomes possible to transfer the 2′-deoxyribose moiety of thymidine (**477**) or the 2′,3′-dideoxyribose moiety in 2′,3′-dideoxyuridine (**497b**) to a series of other bases without the formation of unnatural (and usually biologically inactive) α -nucleosides. Furthermore, modern techniques of attaching enzymes to polymers permit the extensive reuse of these polymeric enzymes. (492a) (For a review on enzyme catalysis, see Ref. 493.)

9. Experimental Conditions

9.1. Sugar Moieties

The crystalline and commercially available sugar moieties such as **18** (mp 133–134°), **17** (mp 81–83°), **24** (mp 110–112°), and **23** (mp 130–132°) as well as 2,3,5-tri-*O*-benzyl-1-*O*-4-nitrobenzoyl-D-arabinofuranose (mp 89–91°) should be checked (mp, TLC) and carefully powdered and dried for 4–18 hours at 40–50°/0.1 mm to remove the last traces of solvent or acetic acid, which can interfere with nucleoside synthesis. If necessary, the crystalline sugar moieties should be recrystallized from methanol and dried subsequently. Sugar **18** should usually be preferred to **17**, since cyclic salts such as **67** with a phenyl substituent are much more stable than those with a methyl substituent as in **27**. Consequently, the thermodynamically controlled formation of *O*-acylated β -nucleosides is more favored with **18**. Furthermore *O*-benzoylated nucleosides usually crystallize much better than the corresponding *O*-acetylated nucleosides. The precious and sensitive **21** gives on recrystallization from anhydrous CCl_4 (100 mL/g) fine colorless needles, which can apparently be stored in a desiccator for months. (494) A new preparation of 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose was recently described. (495)

On reacting 1-*O*-acyl-2-*O*-benzylated D-ribose **502** with $SnCl_4$ in the absence of nucleophilic silylated bases, the resulting 1-cation can undergo a Friedel-Crafts cyclization with the ortho position of the 2-*O*-benzyl group to form the corresponding tricyclic sugar derivative **503** (496-496a) (for other side reactions of sugar moieties in the presence of Lewis acids see Refs. 152b,152c and 256).

502 **503**

9.2. Heterocycles

Whereas *N*-heterocycles such as uracil , thymine, or hypoxanthine are silylated as such and then transformed into the corresponding nucleosides, aminosubstituted heterocycles such as cytosine, adenine, or guanine are much more basic so that the silylated amino-substituted bases form stronger σ complexes with Lewis acid catalysts such as TMSOTf or $SnCl_4$ and thus react more slowly or not at all with sugar moieties than do silylated uracil or thymine.

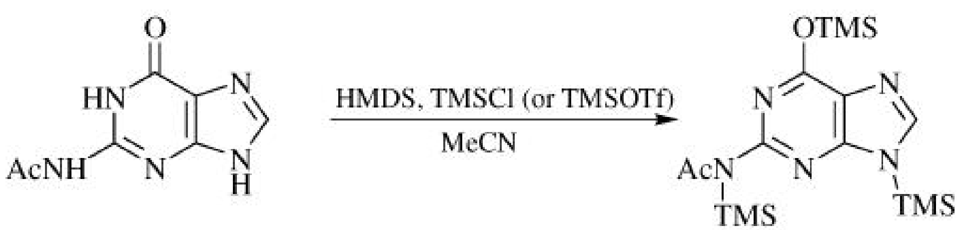
Consequently, the less basic *N*-acylated heterocycles such as N^4-acetyl (or benzoyl)cytosine, (497) N^6-benzoyladenine (mp 243°), (498) or the commercially available (Pharma Waldhof) N^2-acetyl (or N^2-isobutyryl)guanine should usually be preferred since they are also more lipophilic and thus more easily converted to their corresponding silylated derivatives (**97**), **108b**, and **277**, which then form weaker σ complexes with Lewis acids with resulting faster reactions to the desired nucleosides. To enhance the solubility even further, silylated N^2-palmitoylguanine has been employed for transglycosylations (180) instead of silylated N^2-acetyl (or N^2-isobutyryl)guanine. Recently it was observed that 1-*O*-methyl-2-deoxypyranosides condense readily with silylated uracil (**66**) or thymine (**226**) but fail to react with silylated cytosine **222** in the presence of *tert*-butyldimethylsilyl triflate in CH_2Cl_2/acetonitrile. (236) One can assume that, owing to strong σ -complex formation of the basic silylated cytosine **222** with *tert*-butyldimethylsilyl triflate, the reaction of **222** with the intermediate sugar cation was so slow that the sugar cation was converted into the corresponding glycal. (152b,c,236) In the synthesis of hikizimycin, silylated cytosine (**222**) reacts only sluggishly in the presence of TMSOTf. (160) On working with such sensitive 2-deoxysugar moieties, the less basic *N*-acylated aminoheterocycles should always be employed using not only *N*-acetyl or benzoyl substituents but also *N*-*p*-nitrobenzoyl or *N*-trifluoroacetyl groups. The purification of crude heterocycles by silylation and subsequent distillation is briefly discussed in the following section on silylation.

9.3. Silylation

The polar, high melting and rather insoluble heterocyclic bases such as uracil , thymine, N^4-acetyl cytosine, N^6-benzoyladenine, N^2-acetylguanine, or N^2-isobutyrylguanine are transformed on silylation into thermodynamically more stable (78a) lipophilic, basic, and nonpolar volatile silyl derivatives, which are thermally stable but very sensitive to moisture. Of the different silylating agents, HMDS, bp 126° is the most practical and commonly used since only ammonia is evolved on silylation, and excess reagent can be readily removed by evaporation and repeated codistillation with xylene. Even more effective is subsequent Kugelrohr (short path) distillation to give the pure silylated base. With 5-fluorocytosine, the silylated heterocycle was distilled and then recrystallized from heptane. (499) On silylation, distillation and subsequent desilylation with excess water or methanol, crude heterocyclic bases such as adenine can be readily purified. (500) The relatively low rate of silylation with HMDS is accelerated by adding catalytic amounts of acidic catalysts such as $(NH_4)_2SO_4$, TMSCl, or TMSOTf, whereupon ammonium salts such as NH_4Cl will show up in the reflux condenser as well as in the distilled silylated base as a turbid impurity. On silylation of N^4-acetyl cytosine or N^6-benzoyladenine with HMDS in pyridine or in the presence of catalytic amounts of TMSCl, part of the *N*-acyl groups can be lost. (146) Thus samples of silylated *N*-acylated bases should be treated with methanol and subsequently checked by TLC for the potential loss of part of the *N*-acyl groups.

Very insoluble heterocyclic bases such as certain purines can often be silylated only by adding pyridine. Thus if a heterocyclic base does not dissolve after extended heating with HMDS containing catalytic amounts of TMSCl, a polar solvent such as acetonitrile or pyridine should be added, which can then be removed on codistillation with xylene. Other polar solvents such as DMF or *N*-methylpyrrolidone should also be considered as solvents for the silylation of very insoluble heterocyclic bases and the subsequent reaction with protected sugar derivatives such as **18** in the presence of Friedel-Crafts catalysts (see Solvents). (84) It should be realized, however, that DMF and probably also *N*-methylpyrrolidone can react with TMSCl at elevated temperatures (see Solvents).

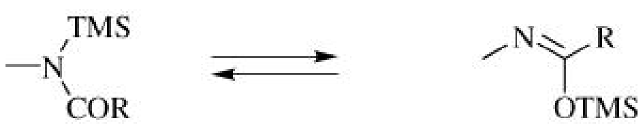
The Langer method of silylation, employing equimolar amounts of HMDS and TMSCl, (501) is also very efficient and quite fast, particularly in acetonitrile at room temperature. The equivalent amounts of NH_4Cl formed are precipitated indicating the progress of silylation. (146) Subsequent filtration of the NH_4Cl with exclusion of moisture and washing with acetonitrile will remove practically all of the NH_4Cl . On Langer silylations in acetonitrile at reflux, the NH_4Cl sublimes nearly quantitatively into the reflux condenser and is thus removed from the reaction. (146) The Langer method transforms *N*-acylated purines such as N^6-benzoyladenine to the corresponding silylated bases such as **97** with minimal cleavage of the corresponding *N*-acyl groups. (146) Thus silylation of N^2-acetylguanine (**303b**) with HMDS and equivalent amounts of TMSCl or TMSOTf gives the silylated N^2-acetylguanine **108b** and NH_4Cl (or ammonium triflate). Silylations with TMSOTf/triethylamine (502) or TMSOTf/DBU (503) have also been described.



303b **108b**

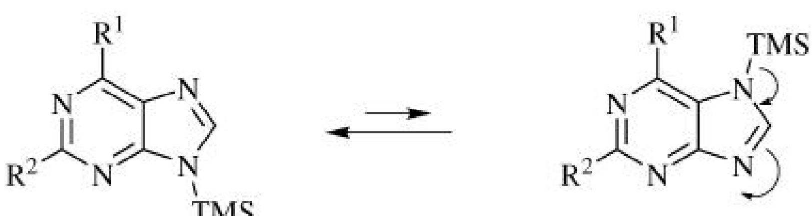
Other silylating agents such as the more expensive BSA or BSTFA silylate heterocyclic bases much faster than HMDS and have thus been used rather frequently. (151,162,239,504–507) During silylation with these reagents, however, *N*-monosilylated or free acetamide or trifluoroacetamide is formed, which can interfere with nucleoside synthesis by competing with persilylated bases for the sugar cation to form protected *N*-acetamides. This problem is particularly important in silylation and nucleoside synthesis in weakly basic systems, such as the preparation of silylated 2,3-diaminomaleodinitrile (DAMN, **130**) or silylated 4,6-diamino-5-nitropyrimidine **464**. Such a side reaction of BSA or *N*-trimethylsilylacetamide was recently observed on silylation of 1,2,4,6-thiatriazin-3-one 1,1-dioxides with BSA followed by reaction with peracylated sugars in the presence of TMSOTf in boiling acetonitrile, which gave only moderate yields of the protected nucleosides and up to 46% of the 1-*N*- β -acetamides of the protected sugars. (162a) Likewise, reaction of 1,3-bis(trimethylsilyl)-1,3,4,7-tetrahydro-2*H*-1,3-diazepin-2-one, prepared in situ with BSTFA, with 1-*O*-methyl-2,3-dideoxy-5-*O*-*p*-toluoyl-D-glyceropentofuranose in the presence of TMSOTf afforded the seconucleoside containing a 1-trifluoroacetamido group in 45% yield. (507a)

Whereas the structures of silylated uracil**66** or thymine **226** are unambiguous, the structures of the silylated N^4-acyl groups in cytosine or the N^2- and N^6-acyl moieties in purines can be formulated as either *N*-silyl **504** or *O*-silyl **505**. (78a,142,508,509) The structure of persilylated N^6-benzoyladenine was recently determined by NMR measurements as having one TMS group at N^9 and the other at the oxygen of the N^6-benzoyl group as in **505**. (509a)



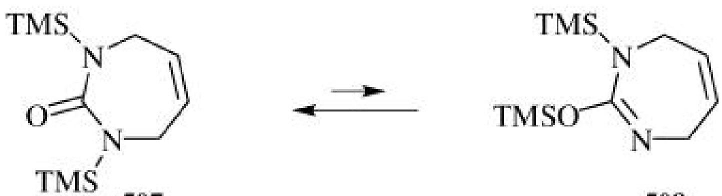
504 **505**

Although silylated purines are usually formulated as the N^9-silylated isomer **108**, it might well be that besides the N^9-silylated purines **108** there are also small amounts of N^7-silylated purines **506** present at equilibrium, (78a,144) which might be the intermediates in the reaction with sugar cations **67** to result in the formation of the N^9-nucleoside.



108 **506**

For a detailed UV, ^{1}H NMR and ^{13}C NMR investigation of the structure of silylated allopurinol, see Ref. (510). Although the structure of the silylated diazepine was determined as **507** by ^{13}C NMR, (511) the heterocycle probably reacts via **508** with sugar cations **67**. For determination of the structure of bis(silylated) 5-methyl-5,6-dihydro-*sym*-triazine-2,4(1*H*,3*H*)dione (**209**), see Ref. 238. (For an alternative formulation of the bis(silylated) heterocycle see Ref. 512.)



507 **508**

9.4. Friedel-Crafts Catalysts

Commercial $SnCl_4$ should be redistilled (bp 114°) with careful exclusion of moisture if the reagent has been stored, to avoid slow nucleoside synthesis or failures. TMSOTf, which can be readily prepared from trifluoromethanesulfonic acid by heating with trimethylsilyl chloride (TMSCl) (131) until HCl evolution ceases, or with tetramethylsilane (513) until methane evolution ceases, should also be redistilled (bp 133–134° or 77°/80 mm) with careful exclusion of moisture, if the reagent has been stored. Trimethylsilyl nonaflate (bp 70°/15 mm) is prepared in similar fashion from nonaflic acid or by in situ reaction of potassium nonaflate with TMSCl in acetonitrile. Other reagents, such as *tert*-butyldimethylsilyl triflate (bp 65–67°/12 mm), (514) are apparently equivalent to TMSOTf in nucleoside synthesis but much more expensive.

Other Friedel-Crafts catalysts such as $TiCl_4$, $BF_3{\cdot}OEt_2$, or TMSI should be redistilled before use. Humid samples of $ZnCl_2$ or $SnCl_2$ or their hydrates can be dehydrated by refluxing with TMSCl, whereupon HCl and hexamethyldisiloxane (bp 101°) are formed. (514a) For comparisons of Friedel-Crafts catalysts in nucleoside synthesis, see Refs. 84,106b,249c, and 514b.

The amount of Friedel Crafts catalyst used depends on the basicity of the silylated base and the sugar (cf **510**) and usually does not exceed 1.2–1.4 equivalents of TMSOTf or $SnCl_4$. Recently it was claimed, however, that 10 equivalents of $SnCl_4$ were necessary for the reaction of 1,3,5-tri-*O*-acetyl-2-deoxy-D-ribofuranose with silylated

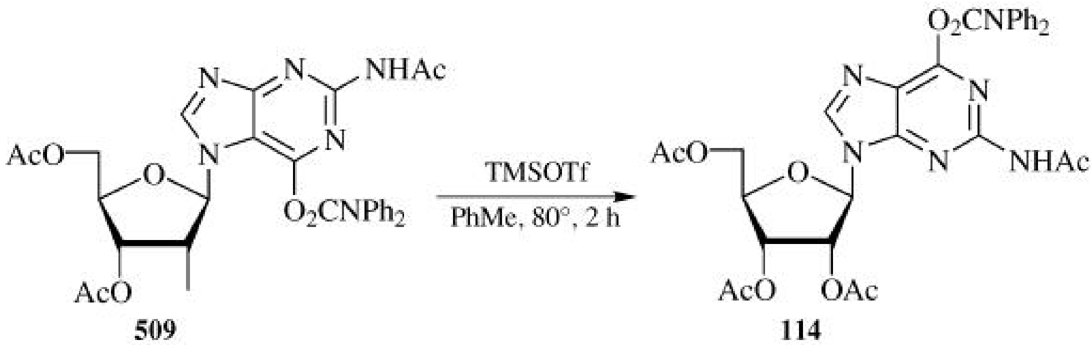
2-*N*-acetyl-6-*O*-diphenylcarbamoylguanine **113** for optimal yields of 2¢-deoxysugars. (515) But in this reaction BSA was used for silylation and it was not stated whether the $SnCl_4$ had been freshly distilled. Since 3,4- or 5-dialkoxyphosphonomethylribofuranosides are partially dealkylated at phosphorus on extended heating with persilylated bases in the presence of TMSOTf in acetonitrile, it is claimed that $SnCl_4$ gives higher yields of di-*O*-alkylated phosphonomethylnucleosides. (515a–d)

9.5. Solvents

Acetonitrile is the most commonly used low-boiling solvent (bp 82°) and is readily purified by heating at reflux over P_2O_5, subsequent distillation, and then distillation over CaH_2. As emphasized in the preparation of protected 6-methyluridine **85**, any impurity will favor the formation of the undesired N^3-nucleoside **86**. There are, however, some good commercial brands of absolute acetonitrile available such as from Merck AG Darmstadt, No. 100004 containing less than 0.005% H_2O, which can be used as such for nucleoside synthesis.

Owing to its polarity, acetonitrile permits homogeneous reactions of polar sugar moieties or silylated pyrimidine bases as well as of their corresponding salts. Acetonitrile also competes with silylated pyrimidine bases for the Lewis acids TMSOTf or $SnCl_4$ to form the corresponding σ complexes. Consequently, the most electron-rich N^1-nitrogen in silylated pyrimidines is only partially blocked by complex formation with TMSOTf or $SnCl_4$, so that the nucleophilic N^1-nitrogen can react with the sugar cation **67** to the desired protected natural N^1-pyrimidine nucleosides. If, however, TMSOTf or $SnCl_4$ blocks most of the N^1 nitrogen of silylated pyrimidines by σ -complex formation, only the less basic and reactive N^3 nitrogen is available to condense with **67** to give the undesired protected N^3-pyrimidine nucleosides.

The much less polar 1,2-dichloroethane, which is readily purified by distillation from P_2O_5 and permits reactions at the boiling point (83°), favors complex formation between the silylated purine moieties and TMSOTf so that the undesired protected N^3- and N^7-purine nucleosides are readily rearranged at 83° to the thermodynamically controlled desired protected natural N^9-purine nucleosides. Since these rearrangements proceed via dissociation of the protected N^3- and N^7-purine nucleosides to the persilylated purine bases and the sugar cations, the more stable sugar cation **67** derived from sugar **18** (compared to the less stable sugar cation **27** derived from sugar **17**) favors these dissociations and resulting rearrangements in 1,2-dichloroethane to the thermodynamically controlled N^9-purine nucleosides. The even less polar toluene (compared to 1,2-dichloroethane) was employed for the rearrangement of the N^7-purine nucleoside **509** to the N^9-purine nucleoside **114**. (141) It can furthermore be assumed that seconucleosides such as **132** or **332** will cyclize on extended heating with TMSOTf in boiling 1,2-dichloroethane



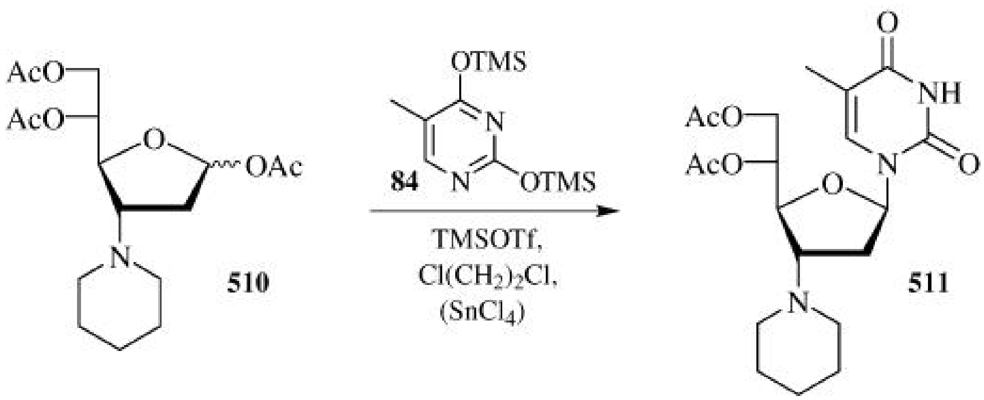
to the ring closed products **131** and **331**. (370) In contrast to these reactions and rearrangements in 1,2-dichloroethane and toluene at higher temperatures, silylated purine bases condense with sugar moieties such as **17** or **18** in acetonitrile in the presence of $SnCl_4$ at ambient temperature to give predominantly the undesired N^7-purine nucleosides. (142) See section on “Mechanism of Pyrimidine and Purine Nucleoside Synthesis.”

Thus acetonitrile is the favored solvent for the TMSOTf or $SnCl_4$ catalyzed reaction of silylated pyrimidine bases with protected sugar moieties such as **18** to give the corresponding protected natural N^1-pyrimidine nucleosides, whereas 1,2-dichloroethane is the preferred solvent for the TMSOTf catalyzed reaction of silylated purine bases with **18** to the protected N^9-purine nucleosides.

Since the reaction temperature in methylene chloride can only be raised to 40°, this solvent is less suitable for the synthesis of purine nucleosides. Chloroform, which is the preferred solvent for the uncatalyzed, (261) CuI, (273) or $ZnCl_2$ (261) catalyzed Silyl-Hilbert-Johnson synthesis of protected 2¢-deoxynucleosides, should be freshly filtered over a small column of activated SiO_2 to remove the alcohol additives and water. Nitromethane, which should be dried with $CaCl_2$ and distilled (bp 101°), has been used as solvent for reactions of protected 1-halosugars with silylated bases in the presence of $AgClO_4$, (74, 80) with 2,4-dimethoxypyrimidine (150) without catalysts as well as with free bases in the presence of $Hg(CN)_2$. (516-518) Nitromethane is comparable to acetonitrile in the reaction of silylated 5-fluorouracil and **18** in the presence of $SnCl_4$, (518) as well as for the synthesis of hikizimycin (**516**). (160) For a recent reaction of 4-amino-3-iodopyrazolo[3,4-*d*]pyrimidine with **18** and $BF_3{\cdot}OEt_2$ in nitromethane, see Ref. 519. Applications of the very polar solvents DMF or *N*-methylpyrrolidone are discussed at the end of this section.

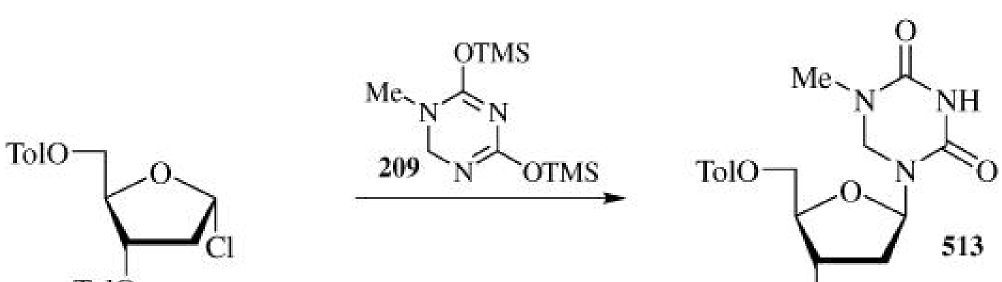
Whereas the rate of the reaction of sugar cations such as **67** with silylated heterocyclic bases is apparently only slightly affected by the solvent, (519a) there are additional factors that can influence nucleoside synthesis.

Consequently, reactions of silylated pyrimidine bases in the presence of TMSOTf or $SnCl_4$ are often attempted in acetonitrile as well as in 1,2-dichloroethane or toluene, since some S_N2 reactions of protected D-arabinose **22** give much higher yields of the desired β -nucleosides in the nonpolar solvents 1,2-dichloroethane (359) and toluene. Likewise, the basic sugar moiety **510** reacts with silylated thymine **84** in 1,2-dichloroethane in the presence of excess TMSOTf to give 31% of the β -nucleoside **511** and 38% of the α -anomer **512**, whereas the same reaction in acetonitrile affords less than 5% of **511** and **512**. (520)



+ α derivative **512**

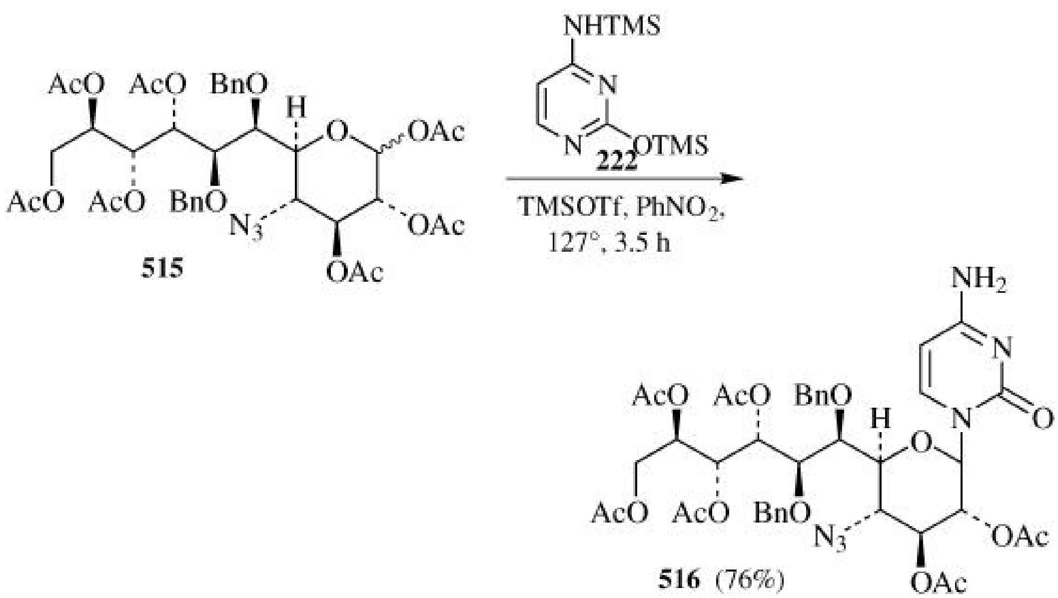
In the reaction of the basic triazine **209** with the standard 2-deoxy sugar **21**, acetonitrile is deemed to be the optimal solvent to obtain the desired protected β -nucleoside **513**: 1,2-dichloroethane and nitromethane give lower yields of **513** and more α -nucleoside **514**. (239)



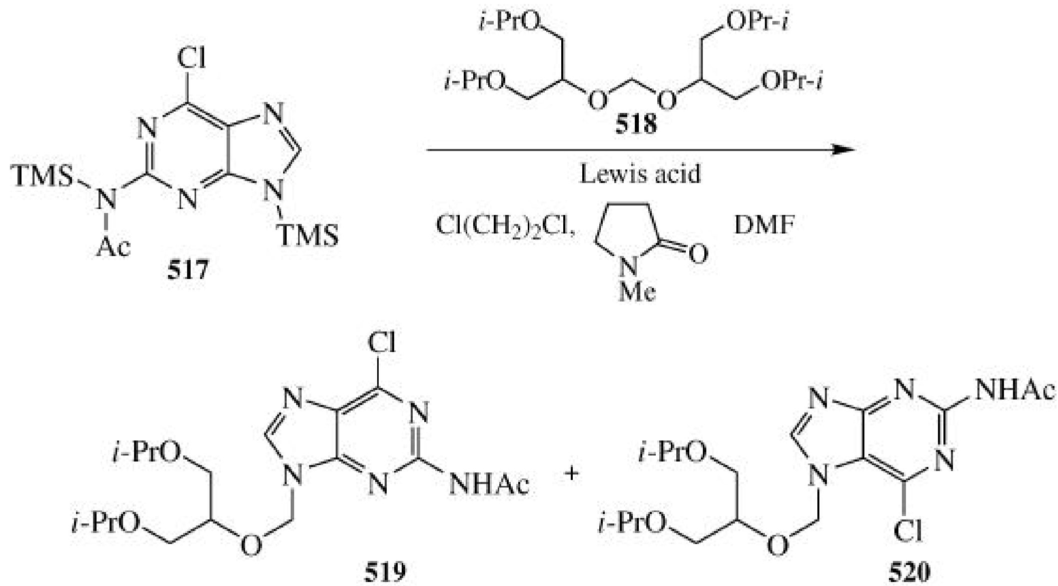
+ α derivative **514**

Protected gemcytabine (**278**) is prepared by heating the sugar moiety **276** with silylated N^4-acetyl cytosine (**277**) in the presence of TMSOTf in 1,1,2-trichloroethane for 18 hours at 113°, whereas in xylene the reaction is complete after 3 hours at 125°. (303) In the synthesis of hikizimycin, the sugar moiety **515** reacts with excess silylated cytosine **222** and TMSOTf in nitrobenzene at 127° to furnish 76% of the protected nucleoside **516**. (160) This reaction, however, might succeed in boiling acetonitrile on employing the less basic silylated N^4-acetyl cytosine **277** instead of **222**.

Silylated 6-chloro-2-acetylaminopurine (**517**) reacts with secosugar **518** at – 30° in 1,2-dichloroethane to give after 2 hours the N^7-nucleoside **520** in 58% yield as well as ca. 6% of the N^9-nucleoside **519**, whereas 6-chloro-N^2,N^9-diacetylpurine affords with secosugar **518** in *N*-methylpyrrolidone or DMF in the presence of $BF_3{\cdot}OEt_2$ or $SnCl_4$ after 4 hours at 100° 58% of the desired N^9-nucleoside **519**. (521) Longer exposure or heating with TMSOTf in 1,2-dichloroethane



might presumably result in the preferential formation of **519**. For recent reviews on the synthesis of seconucleosides such as **160** or **519**, see Refs. 521b–d.



Reaction of neat 1- α -bromo-2-deoxy-2-fluoro-3,5-di-*O*-benzoyl-4-thio-D-arabinofuranoside with neat silylated N^4-acetyl cytosine (**277**) for 8 hours at 80° affords the corresponding protected β -cytidine analog in 33% yield besides 8% of the α -anomer, whereas the same reaction for 48 hours at 80° in 1,2-dichloroethane did not give any nucleoside. (521e)

Possible side reactions of solvents, such as Ritter reactions (199-204) of sugar cations with acetonitrile, should always be considered. Likewise, the very polar solvent DMF (84,86,90,312b,521a) reacts on extended heating with TMSCl to give vinylogous amidinium salts and hexamethyldisiloxane. (522) Finally, one should be aware that 1,2-dichloroethane is carcinogenic to rats and mice at high doses (523) and should therefore only be used in a well ventilated hood. Acetonitrile is likewise considered a toxic hazard (523) and should therefore also be handled with care.

For a general review on the influence of solvents on reactivity, see Ref. (523a).

9.6. Workup of Friedel-Crafts-Catalyzed Silyl-Hilbert-Johnson Reactions

TMSOTf or trimethylsilyl nonaflate are converted on aqueous workup with ice-cold saturated sodium bicarbonate solution into the corresponding sodium salts, which are water soluble and do not interfere with the subsequent extraction of the aqueous phase with CH_2Cl_2. On employing potassium bicarbonate (or carbonate), crystalline potassium nonaflate can be recovered on concentration of the aqueous solution for reuse in the one step-one pot nucleoside synthesis.

In contrast to the use of TMSOTf or nonaflate, the workup of reactions employing $SnCl_4$ (or $TiCl_4$) with ice-cold aqueous sodium bicarbonate usually gives rise to emulsions, which are often difficult to extract with CH_2Cl_2. In these cases, the crude reaction mixture should be filtered through a layer of Celite (or Kieselguhr) to remove the insoluble tin salts, which should be washed thoroughly with CH_2Cl_2. The combined filtrates can then be separated and the aqueous phase extracted with additional volumes of CH_2Cl_2. In certain cases the precipitated tin salts obtained on workup with ethanol/aqueous $NaHCO_3$ solution were subsequently extracted with CH_2Cl_2 in a Sohxlet extractor to avoid any loss of precious substance. (524)

If the $SnCl_4$-catalyzed reactions are run in 1,2-dichloroethane, addition of equivalent amounts of pyridine leads to a colorless precipitate of a pyridine-$SnCl_4$ σ complex, which can be readily filtered through a layer of Celite and washed with 1,2-dichloroethane or CH_2Cl_2. The subsequent workup with ice-cold $NaHCO_3$- CH_2Cl_2 proceeds without complications. (525, 526) Other authors have added an ethanolic solution of triethylamine to the reaction mixture of $SnCl_4$ in 1,2-dichloroethane and then evaporated the volatile fraction. The resulting syrup was stirred in chloroform and evaporated with silica gel, which was then placed on top of a silica gel column for subsequent chromatography. (527, 528) For the synthesis of very acid-sensitive 2-oxo-6-chloropurine nucleosides employing TMSOTf in CH_2Cl_2, pyridine was added to quench the Lewis acid before chromatography on silica. (523b,c)

9.7. Removal of *O*-Acyl, *N*-Acyl, *O*-Benzyl, or *O*-Silyl Protecting Groups

After nucleoside bond formation, workup and crystallization or chromatography followed by crystallization (if they crystallize), the *O*-acyl, *N*-acyl, *O*-benzyl, or *O*-silyl groups are normally removed. *O*-Benzyl groups can be removed by BCl_3 (66,344,349) or BBr_3 (256) at – 78°, by sodium in liquid ammonia, (343) or by hydrogenation. (68, 341) *O*-Silyl groups are usually cleared by treatment with TBAF in tetrahydrofuran, (339, 529) by triethylamine hydrofluoride, by pyridine hydrofluoride, or by treatment with trifluoroacetic acid. (68) For a review of the removal of silyl groups, see Ref. 529a.

The most common procedure used for the removal of *O*- and *N*-acyl groups is transesterification-saponification with saturated methanolic ammonia. On saponification of a protected nucleoside with methanolic ammonia, the progress of the saponification can be followed by TLC or HPLC, whereupon the heterocyclic chromophore can be detected by UV light and the sugar moiety by spraying with 10% H_2SO_4 in ethanol and subsequent heating to 140° to induce darkening of spots containing the carbohydrate moiety. After 72 hours at 24° normally all the *O*- and *N*-acyl groups are removed to give the free nucleoside, which can be checked for purity on SiO_2-TLC plates using the upper phase of *n*-butanol/acetic acid/H_2O (4:1:5) (81) or by RP-HPLC.

In addition to the commonly used methanolic (or ethanolic) ammonia, methylamine, diisopropylamine, triethylamine, and hydrazine have also been employed. (221,298,409,475,530–532) Saponification of 6-(2¢,3¢,5¢-tri-*O*-acetyl- β -D-ribofuranosyl)-6-aza-5,6-dihydro-5,5-dimethyluracil with methanolic ammonia leads to rearrangement of the sugar moiety and gives 6-(β -D-ribopyranosyl)-6-aza-5,6-dihydro-5,5-dimethyluracil. (533)

However, saponification-transesterification with methanolic ammonia can sometimes be quite slow so that even after 72 hours/24° *O*-acylated nucleosides can still be detected by TLC. In the case of 2¢,3¢,5¢-tri-*O*-benzoyl-5-fluorocytidine, the ion exchanger Amberlyst A-26 (OH^- form) in methanol was used to effect a more rapid removal of the *O*-benzoyl groups. (534) Compare also the analogous saponification-transesterification of *O*-acetyl groups with IRA-400 (OH^- form) in methanol. (535) The saponification-transesterification of *O*-acetyl or *O*-benzoyl groups in nucleosides with $NaHCO_3$, Na_2CO_3, or K_2CO_3 in absolute methanol at – 50° was recently suggested. (536-536a) Alternatively, $ZnBr_2$ in chloroform-methanol removes *N*-acyl groups selectively, (536b) whereas lipases selectively saponify *O*-acyl groups. (536c)

After completion of the saponification-transesterification, the methanolic (ethanolic) ammonia (methylamine, diisopropylamine) is evaporated in vacuo. In the case of *O*-benzoyl, 4-nitro, 4-chloro, or 4-methylbenzoyl groups the rates of the saponification-transesterification differ, and the crude product contains the corresponding methyl (or ethyl) benzoates, as well as the corresponding amides, which can be readily extracted with diethyl ether or methyl *tert*-butyl ether.

On using hydrazine benzoate or hydroxylamine acetate in pyridine the more acidic 2¢-*O*-acetates or benzoates can be selectively cleaved to give, with adenosine-2¢,3¢,5¢-tri-*O*-benzoate, a 74% yield of adenosine-3¢,5¢-di-*O*-benzoate. (328, 329, 532, 537) Heating with hydrazine to 100° leads to rapid removal of all *O*-acyl groups. (475)

The standard procedure with methanolic ammonia fails, however, with 5-nitrouridine-tri-*O*-benzoate, (538) which apparently decomposes via addition of NH_3 to the 6-position and subsequent ring opening. Sodium methylate in methanol, however, gives a high yield of 5-nitrouridine. (538-538a) Ammonia and primary or secondary amines in methanol (or ethanol) can aminate (or methoxylate) a 2-chloro or 2-fluoro group, (475, 539) and under forcing conditions, a 6-chloro-, (298) 6-bromo-, or 6-fluoro group in purine nucleosides as well as a 6-fluoro group (540) in pyrimidine nucleosides, whereas NaOH in methanol-H_2O will introduce a methoxy group. (539) Likewise, a 5-trifluoromethyl group in pyrimidine nucleosides is transformed into the corresponding ester moiety, (268) whereas a 5-iodo substituent in a uracilmoiety can be displaced by ethanolic methylamine after 20 hours at 20°. (530) Heating 2-chlorohypoxanthine nucleosides for only 5 minutes at 100° with hydrazine hydrate replaces the chloro group by a hydrazino group. (475) Ester groups react with methanolic ammonia to give the corresponding amide groups as in the synthesis of virazole (**489**) (133, 259) and **186**. 5-Ethoxycarbonyluridine-2′,3′,5′-tri-*O*-acetate is also converted into 5-aminocarbonyluridine by methanolic ammonia. (541) It is of interest that cytidine catalyzes the aminolysis of esters by *n*-butylamine by stabilizing the tetrahedral transition state of aminolysis. (542)

When sodium methylate in methanol is used, treatment of the crude reaction mixture with CO_2 or filtration over a column of Dowex 50 (H^+ form) will neutralize the reaction mixture. The ion exchanger will also remove the sodium ions. On using the sodium methylate/methanol or the sodium benzyl oxide/benzyl alcohol procedure, reactive halogens as in 5,6-dichloropyridazin-3-one (543) or analogous nucleosides (544) are replaced by methoxy or benzyloxy groups.

Since the 2-fluorine moiety in 3′,5′-di-*O*-acyl-2,2′-difluoroadenosine **347** (R^1 = NH_2;R^2 = F) is readily aminated by methanolic ammonia, the more selective saponification of the *O*-acyl groups with lithium hydroxide in acetonitrile-H_2O was applied to afford the free nucleoside in 59% yield. (539) *O*-Benzoylated ribosides of barbituric acid can only be saponified without cleavage of the nucleoside bond by using a very dilute solution of sodium methylate in methanol. (544)

In contrast to methanolic ammonia, saponification with 0.2 N NaOH in THF/MeOH/H_2O (5:4:1) selectively removes the *O*-acetyl moieties in protected cytidines and adenosines, while not affecting the N^4- or N^6-benzoyl groups in the cytosine or adenine moieties. (192)

In 2′-*O*-acetyl-3′-*O*-mesyl-5′-*O*-methoxycarbonyl-1- β -D-xylofuranosylthymine the 2′-*O*-acetoxy group can be selectively removed in 75% yield by treatment with methanolic HCl at 24° for 72 hours. (545) Methanolic HCl also selectively removes the 3′- and 5′-*O*-acetyl groups in 2¢-deoxy-5-(2,2-difluorovinyl)uridine, whereas methanolic K_2CO_3 leads to addition of methanol to the 5-(2,2-difluorovinyl) group. (546, 547) Since methanolic ammonia cleaves the *N*-substituted succinimide ring in 1 β -(2′,3′,5′-tri-*O*-acetyl-D-ribofuranosyl)-1*H*-pyrrole-2,5-dione, methanolic HCl had to be used for the selective removal of the *O*-acetyl protecting groups. (548) The reaction of ammonia with *O*-acyl groups (549) as well as the selective removal of the protecting groups (550) in carbohydrate chemistry has been reviewed.

9.8. Melting Points of Free Nucleosides

Because of the many possible hydrogen bonds between nucleoside molecules in the crystalline state, repeated recrystallization from different solvents or solvent mixtures can give rise to different crystal forms (polymorphism), which have different melting points. Thus one should not be surprised if one obtains crystals with different and usually higher melting points on repeating certain nucleoside syntheses (see the preparation of 6-methyluridine, lumazine riboside, or ribavirin in Ref. 133).

10. Experimental Procedures

Unless indicated otherwise, the following experiments were carried out in a three-neck round-bottom flask equipped with a magnetic stirring bar, dropping funnel, thermometer, reflux condenser, and nitrogen inlet.

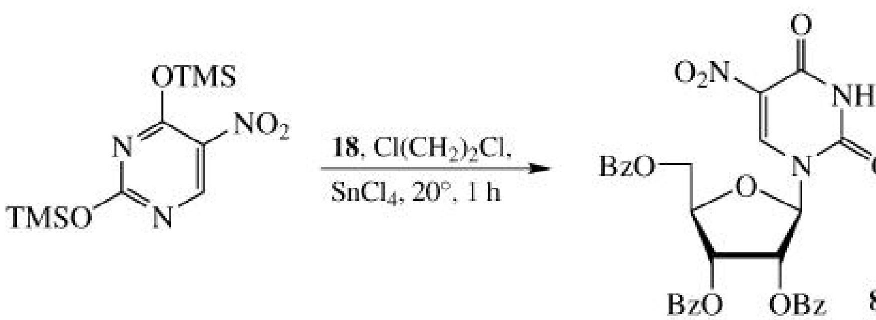
A standard TLC system for analysis of crude protected nucleosides is ethyl acetate:methanol (5:1). Optimal separations of crude protected nucleosides are often observed with two-phase partition systems such as toluene:acetic acid:H_2O (5:5:1) or *n*-butyl acetate:methyl glycol:H_2O (4:1:2) for the protected nucleosides, whereas the free nucleosides often show good separations with the two-phase system *n*-butanol:acetic acid:H_2O (5:1:4). In order to obtain reproducible results, the two-phase systems should be placed into the chromatography vessel. To avoid any contact of the silica layer of the TLC plates with the stationary aqueous lower phase, the lower part of the silica plates should be scraped off so that the silica layer will only come in contact with the upper, mobile phase of these partition systems. (81, 84)

The best analytical, as well as preparative, separations of mixtures of free, unprotected nucleosides (especially mixtures of α / β anomers) can be achieved by HPLC on reversed phase (RP) columns (e.g., Nucleosil 7 C_{18} columns) using linear gradients of 100 to 50% water with 0 to 50% methanol or acetonitrile.

For supplies of special carbohydrate building blocks or larger amounts of particular carbohydrate derivatives such as **18, 17**, or N^2-acetylguanine (**303b**) contact:

Ajinimoto Co., Inc. 1–15–1 Kyobashi, Chuo-ku, Tokyo 104, Japan
Phone + 81–3-5250–8111; Fax + 81–3-5250–8293
Berry & Assoc., Inc. P.O. Box 1071, Ann Arbor, MI 48106, USA
Phone + 1–734–426–3787, Fax + 1–734–426–9077
Boehringer Ingelheim KG, Chem. Division, Bingerstr. 137, 55216 Ingelheim, Germany
Phone + 49–6132–772192; Fax + 49–6132–773755
Cambridge Research Biochemicals, Gadbrook Park Northwich, Cheshire CW9 7RA, U.K.
Phone + 44–606–41100; Fax + 44–606–49366
Omnichem S. A., Indust. Res. Park-Fleming, 1348 Louvain-La Neuve, Belgium
Phone + 32–10–483111; Fax + 32–10–450693
Pharma-Waldhof GmbH, Postfach 110732, 40507 Düsseldorf, Germany

Phone + 49–211–526020; Fax + 49–211–5260211
Pro.Bio.Sint S.r.I., Via Valverde 20/22, 21100 Varese, Italy
Phone + 39–332–218136; Fax + 39–332–212575
Pfanstiehl Laboratories, Inc., 1219 Glen Rock Avenue, Waukegan, IL 60085–0439, USA
Phone + 1–800–383–0126, Fax + 1–708–623–9173M
Reliable Biopharmaceutical Corp., P.O. Box 2517, St. Louis, MO 63114, USA
Phone + 1–314–429–7700, Fax + 1–314–429–0937
Yamasa Corporation, 1–23–8 Kakigarocho, Nihonbashi, Chuo-Ku, Tokyo 103, Japan
Phone + 81–3-3668–3366; Fax + 81–3-3668–3177



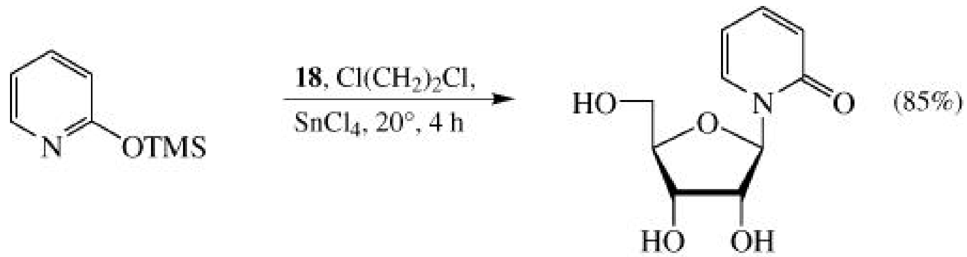
(96%)

81a

10.1.1. 2',3',5'-tri-O-benzoyl-5-nitrouridine (81a) (84)

A mixture of 7.85 g (50 mmol) of 5-nitrouracil, 42 mL (200 mmol) of HMDS, and 1 mL of TMSCl was heated at reflux for 1 hour, whereupon the 5-nitrouracil had passed into solution. The excess HMDS (bp126°) was removed by distillation and the residue was distilled at 110–111° (0.2 Torr) in a Büchi-Kugelrohr short-path distillation apparatus with careful exclusion of moisture to afford 14.3 g (95%) of silylated 5-nitrouracil (80) as a viscous liquid. This product was dissolved in 100 mL of 1,2-dichloroethane (distilled from P_4O_{10}) to give a 475 mM standard solution.

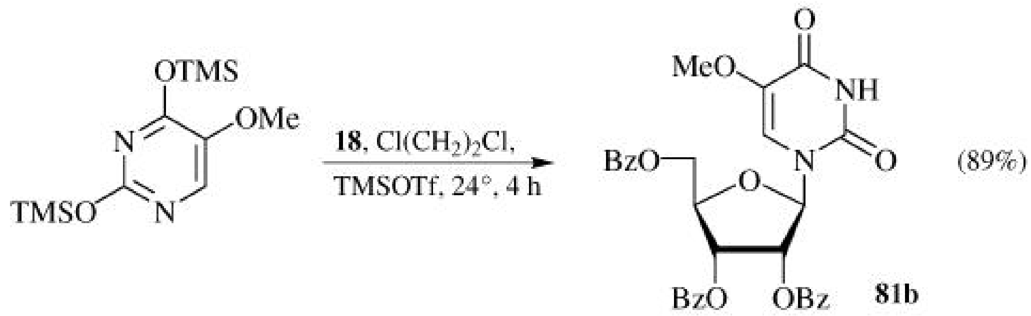
To a solution of 5.04 g (10 mmol) of **18** in 75 mL of 1,2-dichloroethane, 23 mL (11 mmol) of a standard solution of silylated 5-nitrouracil in 1,2-dichloroethane and 0.35 mL (3 mmol) of redistilled (bp114°) $SnCl_4$ in 40 mL of 1,2-dichloroethane were added with stirring. After 1 hour the reaction mixture was diluted with 150 mL of CH_2Cl_2 and shaken with 200 mL of saturated $NaHCO_3$. After filtration through a layer of Celite to remove the tin salts and repeated washings of the Celite layer with CH_2Cl_2, the layers were separated and the aqueous phase was extracted with 3 × 100 mL of CH_2Cl_2. The combined organic phase was dried (Na_2SO_4) and evaporated to give 6.9 g of crude product, which was recrystallized from 200 mL of ethanol to furnish in four crops 5.79 g (96%) of pure 2′,3′,5′-tri-*O*-benzoyl-5-nitrouridine (**81a**), mp 184–185°.



10.1.2. 1- β -D-Ribofuranosyl-2-pyridin-2-one (99)

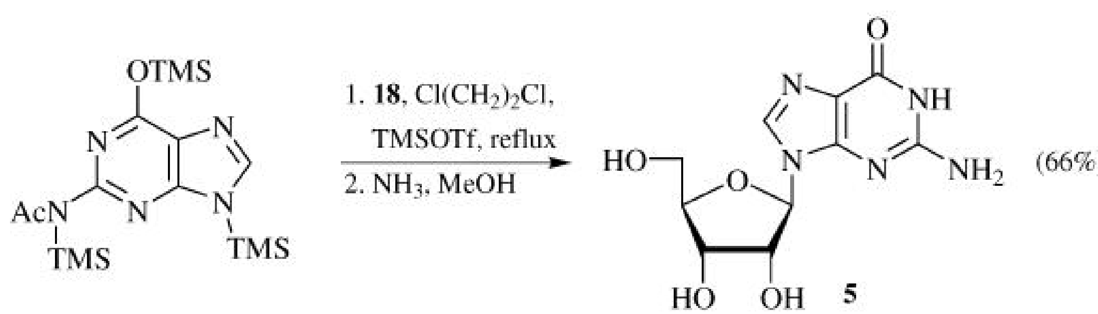
A mixture of 9.51 g (100 mmol) of purified pyridin-2-one and 80 mL (400 mmol) of HMDS was heated at reflux for 1 hour in an oil bath with magnetic stirring and evolution of NH_3, whereupon the heterocyclic base passed into solution. After distillation of the excess HMDS, the residue was distilled in a Büchi short-path Kugelrohr apparatus at 65°/12 mm to afford 15.9 g (95%) of 2-trimethylsilyloxypyridine, which was dissolved in 200 mL of 1,2-dichloroethane. After addition of 50.4 g (100 mmol) of **18**, a solution of 14.0 mL (120 mmol) of redistilled (bp114°) $SnCl_4$ in 300 mL of 1,2-dichloroethane was added rapidly with stirring and exclusion of moisture. After 4 hours the reaction was practically complete according to TLC [upper phase of toluene:acetic acid:H_2O (5:5:1)]. The reaction mixture was poured onto a mixture of 600 mL of ice-cold CH_2Cl_2 and 750 mL of saturated $NaHCO_3$ solution. The crude reaction mixture was filtered through a layer of Celite, and the Celite layer was carefully washed with CH_2Cl_2. The filtrate layers were separated and the aqueous phase was extracted with 4 × 250 mL of CH_2Cl_2. The combined organic phase was dried (Na_2SO_4) and evaporated to give 62 g of a crude oil, which was recrystallized from 900 mL of CCl_4 to give in several crops 45.6 g (85%) of pure 1-(2′,3′,5′-tri-*O*-benzoyl-β-D-ribofuranosyl)pyridin-2-one, mp 140–142°.

The 2′,3′,5′-tri-*O*-benzoate (2.75 g, 5 mmol) was dissolved in 150 mL of saturated methanolic ammonia, stirred for 24 hours at 24°, and evaporated. The residue was dissolved in 100 mL of H_2O and the aqueous phase was extracted with 3 × 75 mL of methyl *tert*-butyl ether to remove the methyl benzoate and benzamide. The aqueous solution was evaporated and the residue was recrystallized from 20 mL of ethanol: 2-propanol (3:1) to give in two crops 0.9 g (80%) of 1- β-D-ribofuranosyl-2-pyridin-2-one, mp 147–150°.



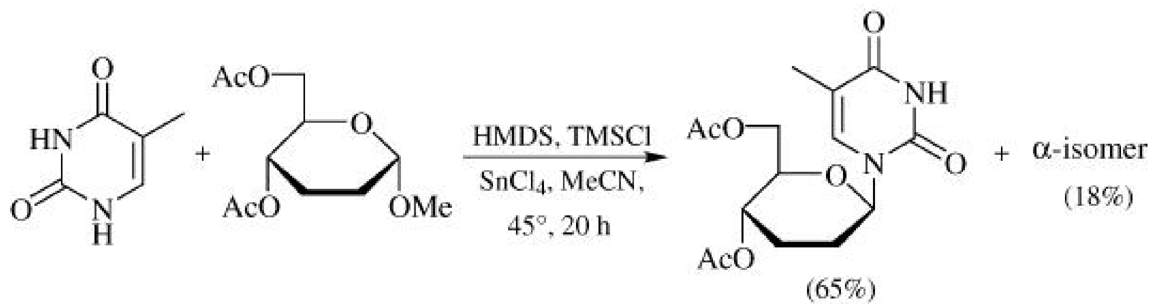
10.1.3. 5-Methoxyuridine-2′,3′,5′-tri-O-benzoate (81b) (133, 189)

(a) To a stirred solution of 5.04 g (10 mmol) of **18** in 75 mL of 1,2-dichloroethane, 34 mL of a 0.356 N standard solution (11 mmol) of silylated 5-methoxyuracil ((80)) in 1,2-dichloroethane and 22.8 mL of a 0.522 N standard solution of TMSOTf in 1,2-dichloroethane were added under nitrogen with exclusion of moisture. After 4 hours at 24° and dilution with CH_2Cl_2, the solution was shaken with excess ice-cold saturated $NaHCO_3$ solution and the aqueous phase was extracted with 3 × 50 mL of CH_2Cl_2. The combined organic phase was dried (Na_2SO_4) and evaporated to afford the crude protected nucleoside, which crystallized from ethyl acetate-hexane to give 5.24 g (89%) of pure crystalline **81b**, mp 205–207°, homogeneous on TLC (ethyl acetate:methanol 5:1). (b) To a mixture of 0.53 g (5 mmol) of 5-methoxyuracil, 2.52 g of **18**, and 3.84 g (12 mmol) of potassium nonaflate ($C_4F_9SO_3K$) in 50 mL of acetonitrile were added 0.74 mL (3.5 mmol) of HMDS and 1.89 mL (15 mmol) of trimethylchlorosilane. The mixture was heated at reflux for 20 hours. After workup with ice-cold $KHCO_3$/ CH_2Cl_2, the biphasic mixture was filtered to afford ~ 3 g (80%) of recovered potassium nonaflate. The combined organic phase was dried (Na_2SO_4) and evaporated, and the crude product was recrystallized from ethyl acetate-hexane to give 2.09 g (71%) of pure crystalline 5-methoxyuridine-2′,3′,5′-tri-*O*-benzoate (**81b**), mp 205–207°.



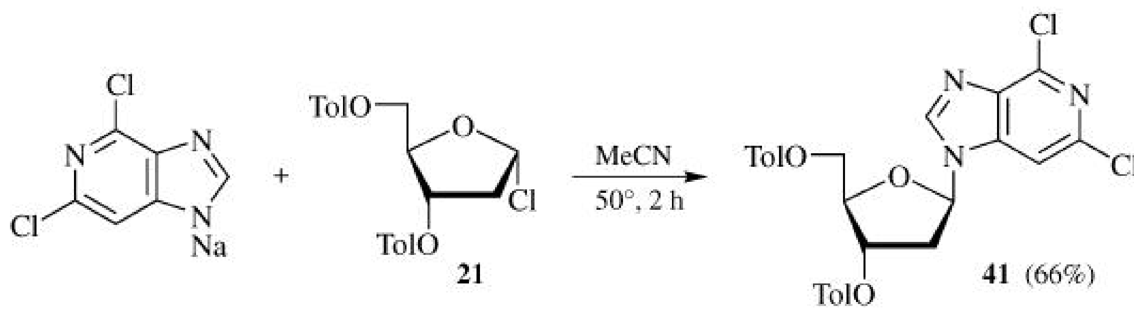
10.1.4. Guanosine (5) (133)

To a stirred mixture of 13.5 mL (4.09 mmol) of a 0.303 N standard solution of silylated N^2-acetylguanine (**108b**) in 1,2-dichloroethane and 1.86 g (3.7 mmol) of **18** in 35 mL of 1,2-dichloroethane was added 6.32 mL (4.46 mmol) of a 0.705 N standard solution of TMSOTf in 1,2-dichloroethane. The reaction mixture was heated at reflux for 1.5–4 hours, and then diluted with CH_2Cl. On workup with ice-cold $NaHCO_3$ solution, there was obtained 2.32 g of crude product, which was kept for 42 hours in 125 mL of methanolic ammonia at 24°. After workup, recrystallization from H_2O gave, in two crops, 0.69 g (66%) of pure guanosine, which was homogeneous (R_f 0.3) in the partition system *n*-butanol:acetic acid:H_2O (5:1:4) and whose ^1H NMR spectrum at 400 MHz in D_2O showed only traces of the undesired N^7-anomer of guanosine.



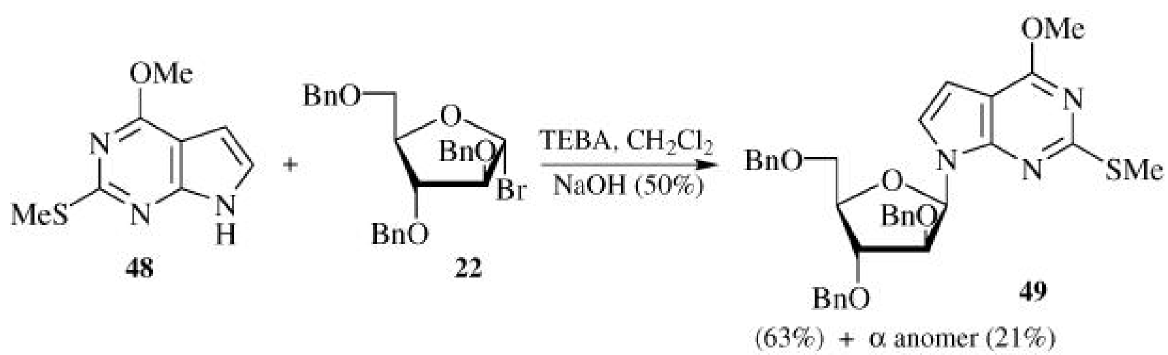
10.1.5. 1-(4',6'-di-O-acetyl-2',3'-dideoxy- β -and- α -D-glucopyranosyl)thymine (192)

To a stirred suspension of 2.15 g (8.75 mmol) of pure oily methyl 4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside, 1.21 g (9.5 mmol) of thymine, and 2.0 mL (9.59 mmol) of HMDS in 70 mL of acetonitrile, 1.35 mL (10.5 mmol) of trimethylchlorosilane, and 1.3 mL (11 mmol) of redistilled $SnCl_4$ were added carefully. The reaction mixture was heated at 44° for 22 hours, then evaporated in vacuo. The crude product was taken up with 150 mL of ice-cold ethyl acetate and 100 mL of saturated $NaHCO_3$ solution. After filtration through a layer of Celite, the aqueous phase was extracted with 2 × 150 mL of ethyl acetate, and the combined ethyl acetate solution was washed with 150 mL of saturated NaCl solution, dried (Na_2SO_4), and evaporated to give 2.5 g of crude product, which contained four compounds (TLC, EtOAc). Chromatography on a 5 × 36-cm column of SiO_2 and elution with hexane:ethyl acetate (3:1) afforded 1.93 g (65%) of 1-(4,6-di-*O*-acetyl-2′,3′-dideoxy- β -D-glucopyranosyl)thymine and 0.53 g (18%) of 1-(4,6-di-*O*-acetyl-2′,3′-dideoxy- α -D-glucopyranosyl)thymine as well as 4% of the corresponding N^3- β and 4% of the N^3- α -nucleosides.



10.1.6. 2,6-Dichloro-1-(2'-deoxy-3',5'-di-O-p-toluoyl-β-D-erythro-pentofuranosyl)imidazo-[4,5-c]pyridine (41) (64)

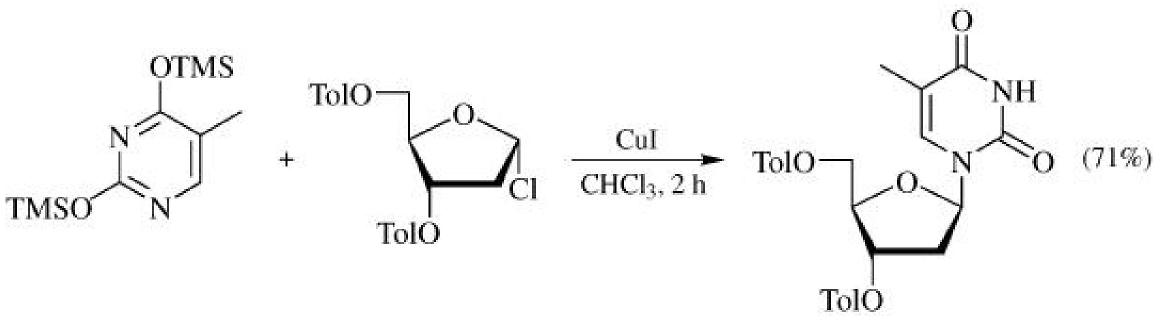
To a stirred suspension of 0.61 g (3.2 mmol) of 2,6-dichlorimidazo-[4,5-*c*]pyridine in 25 mL of acetonitrile was added 0.17 g (3.5 mmol) of 50% oily immersion of NaH under nitrogen. After 30 minutes at room temperature, 1.38 g (3.5 mmol) of **21** was added and the reaction mixture was stirred for 2 hours at 50°. Filtration and evaporation of the filtrate afforded the crude oily product, which was chromatographed in toluene:acetone (95:5) on a 4 × 40-cm column of SiO_2 to give 1.15 g (66%) of pure **41**, mp 165–167°.



10.1.7. 4-Methoxy-2-(methylthio)-7-(2',3',5'-tri-O-benzyl-β-D-arabinofuranosyl)pyrrolo-[2,3-d]pyrimidine (49) (66)

Dry hydrogen bromide was bubbled into a solution of 3.5 g (6.15 mmol) of commercial 1-*O*-*p*-nitrobenzoyl-2,3,5-tri-*O*-benzyl-D-arabinofuranose (Pfanstiehl Laboratories, Inc.) in 15 mL of dry CH_2Cl_2 until no further *p*-nitrobenzoic acid precipitated. The acid was filtered and washed with a small volume of dry CH_2Cl_2 and the combined filtrate was evaporated to give **22**. The 1-bromosugar **22** was dissolved in 10 mL of CH_2Cl_2 and added to a suspension of 1.0 g (5.1 mmol) of 4-methoxy-2-(methylthio)-7*H*-pyrrolo[2,3-*d*]pyrimidine (48) in 10 mL of CH_2Cl_2.

After addition of 0.3 g (1.1 mmol) of benzyltriethylammonium chloride and 30 mL of 50% NaOH, the mixture was stirred vigorously for 15 minutes with a vibromixer. The organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated. The viscous residue was chromatographed using $CHCl_3$ on a 5 × 70-cm column of SiO_2. After elution of 0.63 g (21%) of the pure α anomer **50**, mp 62–63° (methanol), 1.94 g (63%) of the desired viscous β anomer **49** was obtained.



10.1.8. 3',5'-Di-O-toluoylthymidine (273)

To a stirred solution of 1.2 g (3.1 mmol) of **21** and 1.0 g (3.4 mmol) of bis(trimethylsilyloxy)thymine in 80 mL of dry $CHCl_3$, 0.60 g (3.1 mmol) of anhydrous CuI was added. After 2 hours the reaction mixture was treated with 60 mL of saturated $NaHCO_3$ solution and filtered through a layer of Celite. After reextraction of the aqueous phase with 50 mL of CH_2Cl_2, the combined organic phase was dried (Na_2SO_4) and concentrated to give 1.4 g (92%) of a white solid with a β : α ratio of 93:7 (^{1}H NMR). Stirring of the solid with 40 mL of ethanol, filtration, and washing with 2 × 15-mL portions of ethanol gave 1.1 g (71%) of the pure β anomer, mp 195–196°.

11. Tabular Survey

The following tables include examples of nucleoside synthesis collected during the last 20 years up to the middle of 1994. Subsequently only a few additional papers and patents are cited. Searches were conducted in the *Chemical Abstracts* databases and the *Science Citation Index*. Because of the enormous extent of literature dealing with the synthesis of nucleosides, however, this comprehensive collection of data cannot be guaranteed complete.

The tables include reactions of free sugars or sugar derivatives with heterocyclic bases and their derivatives. Transglycosidation reactions as well as reactions of sugars to build up the pyrimidine or purine part of the nucleosides, such as the “Sanchez-Orgel”-type reaction, are **not** part of the tables but are covered in the text.

The tabular survey is divided in the following headings:

Within each table, sugar derivatives reacting with heterocyclic bases are listed according to increasing carbon number, and increasing hydrogen number within a given carbon number.

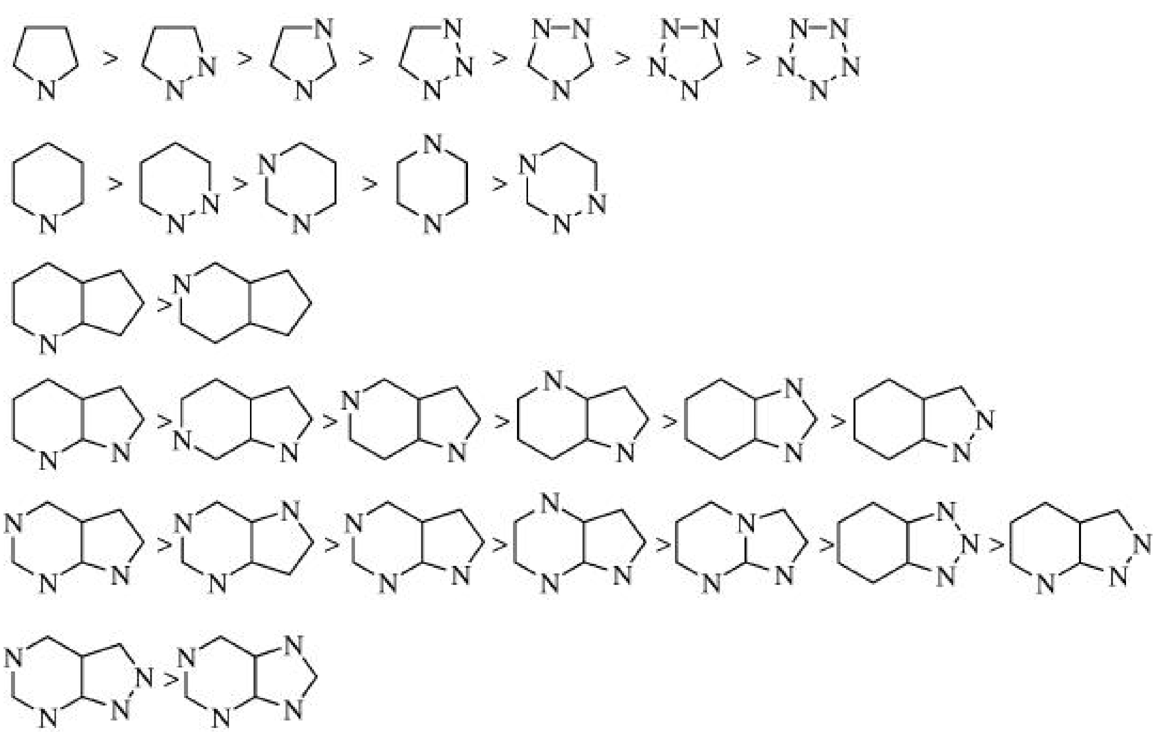
For sugar derivatives having the same carbon and hydrogen number, the sugars are listed according to increasing ring size. The order of the reactants (heterocycles) is as follows:

Number of Rings

Ring size (5-ring > 6-ring ..)

Number of N atoms in the Ring (pyridine > pyrimidine…)

N-pattern in the heterocycles



⇅

Number of substituents

⇅

Kind of substituents:
F > Cl > Br > I > CO > NHR > NR_2 > OH > NO_2 > CN > Alkyl > Aryl > O-Alkyl > CONR > CO_2R > S-Alkyl > Acetyl > Benzoyl
Yields are given in parentheses in the product column of the tables.

Abbreviations:

Aliquat 336	methyltrioctylammonium chloride
An	anisoyl
BETF	2-(1-benzimidazoyl)-3-ethylbenzoxazolium tetrafluoroborate
Bn	benzyl
BOC	*tert*-butoxycarbonyl
BSA	*N,O*-bis(trimethylsilyl)acetamide
Bz	benzoyl
t Bz	*p*-*tert*-butylbenzoyl
Cbz	carbobenzyloxy
CETF	2-chloro-3-ethylbenzoxazolium tetrafluoroborate
DEAD	diethyl azodicarboxylate
DIAD	diisopropyl azodicarboxylate
DMAP	4-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMTST	dimethyl(methylthio)sulfonium triflate
FMPT	2-fluoro-1-methylpyridinium tosylate
HMDS	hexamethyldisilazane
HMPA	hexamethylphosphortriamide
IDCP	iodonium dicollidine perchlorate
MMTrO	*p*-monomethoxytrityl
Ms	mesyl
MS	molecular sieves
NBS	*N*-bromosuccinimide
NIS	*N*-iodosuccinimide

NMP	*N*-methylpyrrolidone
NPht	phthalimide
Piv	pivaloyl
Pht	phthaloyl
Py	pyridine
TBDMSO	*tert*-butyldimethylsilyloxy
TBDPSO	*tert*-butyldiphenylsilyloxy
TEBA	benzyltriethylammonium chloride
TFA	trifluoroacetic acid
Tf	trifluoromethylsulfonyl (triflyl)
Tf_2O	trifluoromethylsulfonic acid anhydride
$TIPDSCl_2$	1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane
TMS	trimethylsilyl
TMSCl	trimethylsilyl chloride
TMSI	trimethylsilyl iodide
TMSOTf	trimethylsilyl triflate
Tol	toluoyl
Tr	triphenylmethyl
TsOH	*p*-toluenesulfonic acid
Ts	tosyl

Table I. One Step-One Pot Silylation/Coupling of Heterocyclic Bases with Sugars– Friedel-Crafts Catalysts

View PDF

Table II. One Step-One Pot Coupling of Heterocyclic Bases with Sugars– Friedel-Crafts Catalysts

View PDF

Table III. Reactions of Silylated Heterocyclic Bases with Protected Sugars - $SnCl_4$ Catalyst

View PDF

Table IV. Reactions with Trimethylsilyl and Silver Triflates and Perchlorates

View PDF

Table V. Reactions with Titanium Tetrachloride as Catalyst

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Table VI. Reactions with Boron Trifluoride Etherate as Catalyst

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Table VII. Reactions with Miscellaneous Friedel-Crafts Catalysts

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Table VIII. Reactions of Silylated Bases with Protected Sugars with or without Catalysts

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Table IX. Fusion Reactions

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Table X. Miscellaneous Reactions of Heterocyclic Bases with Protected Sugars

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Table XI. Reactions of Acidic Heterocycles with 1-Halosugars in the Presence of Bases

View PDF

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS

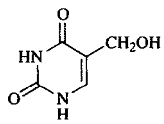
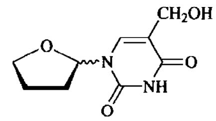
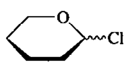
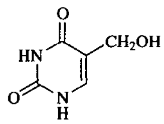
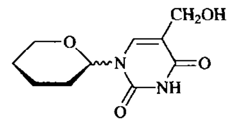
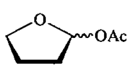
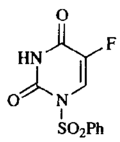
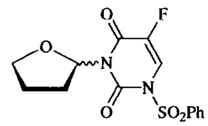
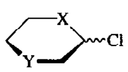
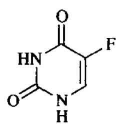
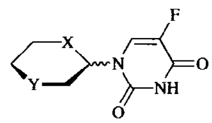
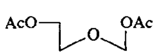
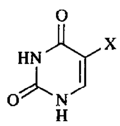
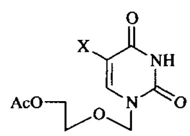
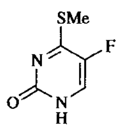
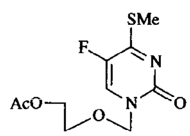
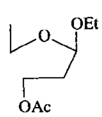
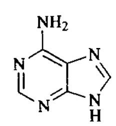
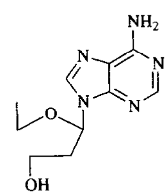
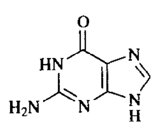
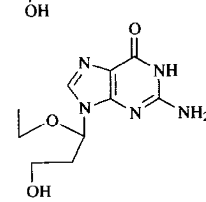
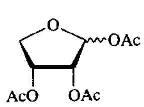
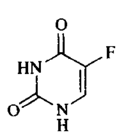
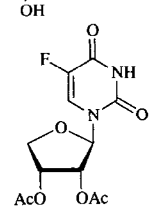
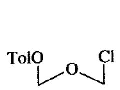
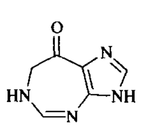
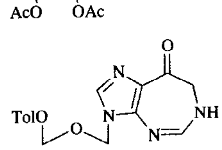
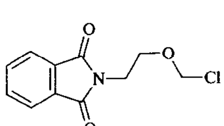
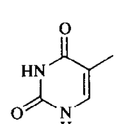
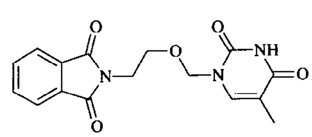
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		TCS, HMDS 1. 160° 2. rt, 24 h	 (40)	551
C_5 		TCS, HMDS 1. 160° 2. rt, 24 h	 (61)	551
C_6 		BSA, $SnCl_4$, CH_2Cl_2, rt, 4 h	 (88)	552
		TCS, HMDS, $SnCl_4$, MeCN, 0°, 30 min	 X Y O S (65) S O (82)	553
C_7 		BSA, $SnCl_4$, CH_2Cl_2, rt, 12 h	 X F (53) Br (57) I (75)	554
		BSA, $SnCl_4$, CH_2Cl_2, rt, 12 h	 (84)	554
C_9 		1. HMDS, $(NH_4)_2SO_4$, TMSOTf, MeCN, 20°, 16 h 2. NH_3, MeOH	 (50)	555
		1. HMDS, $(NH_4)_2SO_4$, TMSOTf, MeCN, 20°, 16 h 2. NH_3, MeOH	 (50)	555
C_{10} 		1. BSA, MeCN, 50°, 3 h 2. $SnCl_4$, rt, 12 h	 (28)	556
		BSA, Py, MeCN, $SnCl_4$, $Cl(CH_2)_2Cl$	 (27)	557
C_{11} 		TCS, HMDS, TsOH, MeCN, reflux 19 h	 (88)	558

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

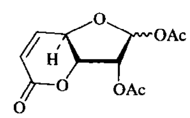
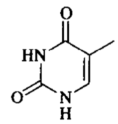
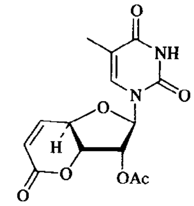
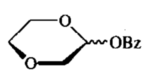
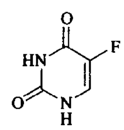
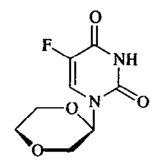
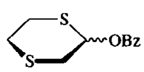
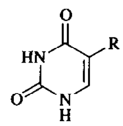
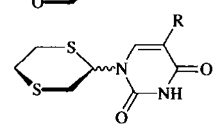
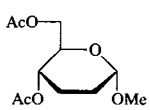
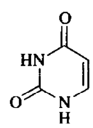
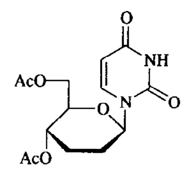
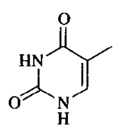
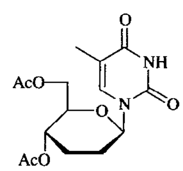
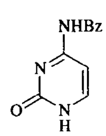
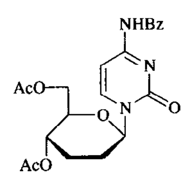
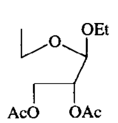
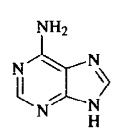
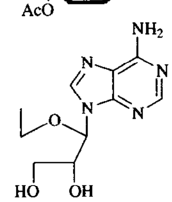
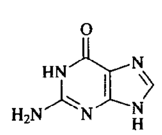
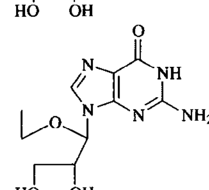
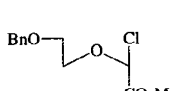
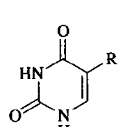
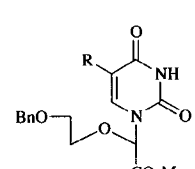
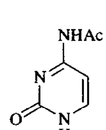
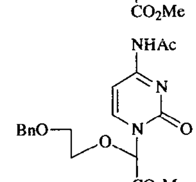
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TCS, HMDS, $SnCl_4$, MeCN, 120°, 30 min	 (60)	559
		TCS, HMDS, $SnCl_4$, MeCN, 0°, 30 min	 (70)	553
		TCS, HMDS, $SnCl_4$, MeCN, 0°, 30 min	 R: H (59); Me (67)	553
		TCS, HMDS, $SnCl_4$, MeCN, 45°, 20 h	 (60) + α anomer (18)	192
		TCS, HMDS, $SnCl_4$, MeCN, 45°, 20 h	 (65) + α anomer (18) + N^3-β isomer (4) + N^3-α isomer (4)	192
		BSA, $SnCl_4$, MeCN, 45°, 2 h	 (50) + α anomer (20)	192
		1. HMDS, $(NH_4)_2SO_4$, TfOH, MeCN, 20°, 16 h 2. NH_3, MeOH	 (40)	555
		1. HMDS, $(NH_4)_2SO_4$, TfOH, MeCN, 20°, 16 h 2. NH_3, MeOH	 (61)	555
C_{12} 		BSA, $SnCl_4$, CH_2Cl_2, 0-25°, 17 h	 R: H (85); F (66)	560
		BSA, $SnCl_4$, CH_2Cl_2, 0-25°, 17 h	 (71)	560

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

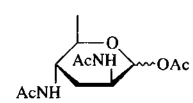
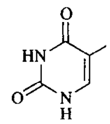
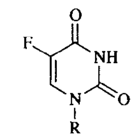
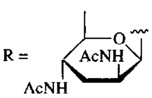
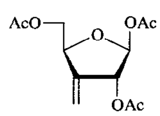
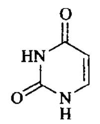
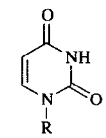
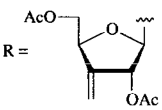
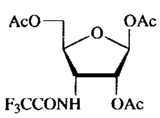
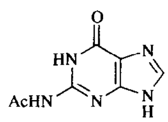
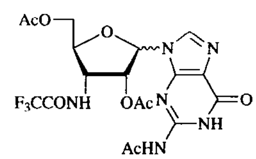
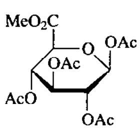
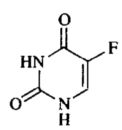
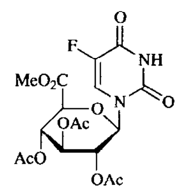
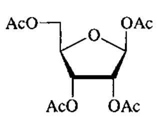
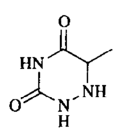
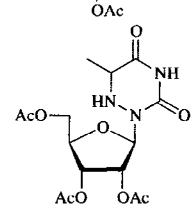
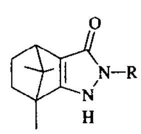
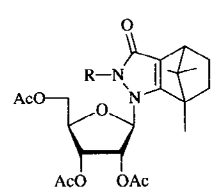
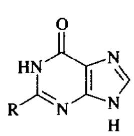
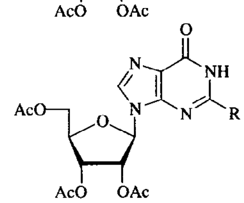
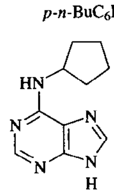
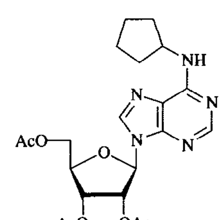
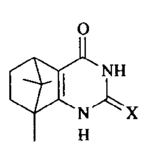
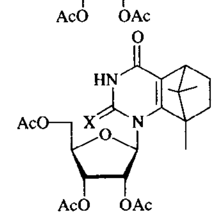
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		BSA, $SnCl_4$, MeCN, rt, 1 h	 (71) R = 	561
		TCS, HMDS, TMSOTf, $Cl(CH_2)_2Cl$, 60°, 2 h	 (64-70) R = 	562
C_{13}				
		TCS, HMDS, $C_4F_9SO_3K$, MeCN, reflux, 24 h	 (70) α:β = 1:2.5	563
		TCS, HMDS, $SnCl_4$, MeCN, rt, 10 h	 (80)	767
		TCS, HMDS, TMSOTf, $Cl(CH_2)_2Cl$, 0°, 24 h (Ar)	 (10)	565
		TCS, HMDS, $SnCl_4$, MeCN, rt, time	 R: Ph, time 19 h (30); p-ClC_6H_4, time 13 h (33)	566
		BSA, TMSOTf, MeCN		
	R			
	AcNH	heat, 8 h	(70) + 5% N^7-β isomer	190
	Br	reflux, 15 min	(75)	190
	p-n-BuC_6H_4NH	heat, 8 h	(69) + 11% N^7-β anomer + 11% N^7-β isomer	190
	p-n-BuC_6H_4NH	reflux, 7 h	(69) + 11% N^7 isomer	505
		TMSOTf, dioxane (N_2) rt, 1 h	 (41)	567
		TCS, HMDS, $SnCl_4$, MeCN, rt, time	 X: O, time 18 h (31); S, time 20 h (28)	566, 566

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS *(Continued)*

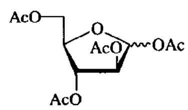
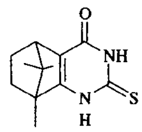
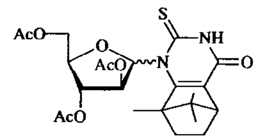
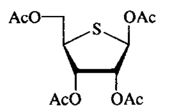
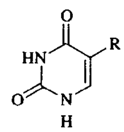
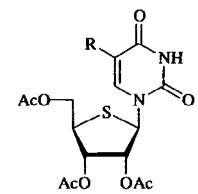
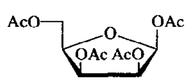
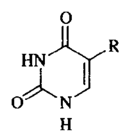
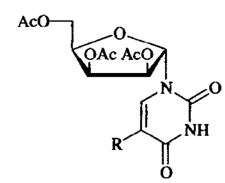
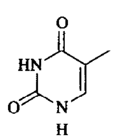
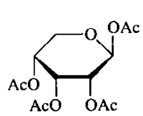
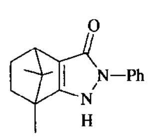
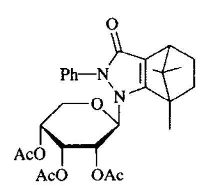
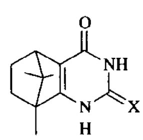
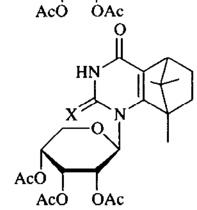
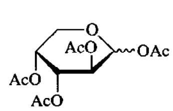
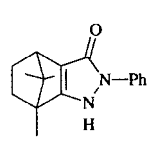
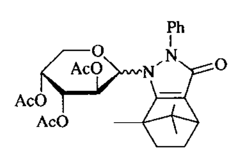
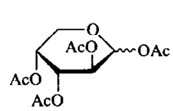
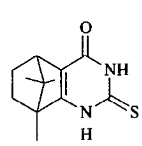
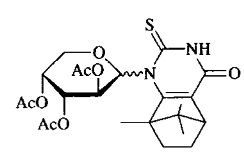
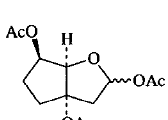
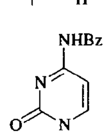
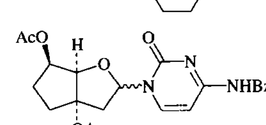
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TCS, HMDS, $SnCl_4$, MeCN, rt, 17 h	 (26)	566
		TCS, HMDS, CF_3SO_3H, MeCN	 R: H, 80°, 3 h (41); F, 25°, 24 h (48); Me, 80°, 3 h (38); NO_2, 25°, 24 h (55)	568 568 568 568
		TCS, HMDS, $SnCl_4$	 I	
	R: H	MeCN, rt, 22 h	(49) + 14% N^3-isomer + 11% N^1,N^3-bisisomer	537
	R: Me	MeCN, heat, 25 min	(—)	537
		TCS, HMDS, $SnCl_4$, MeCN, reflux 1 h	I, R = Me, (—) + N^3-isomer	537
		TCS, HMDS, $SnCl_4$, MeCN, rt, 24 h	 (31)	566
		TCS, HMDS, $SnCl_4$, MeCN, rt, 21 h	 X: O (29); S (31)	566
		TCS, HMDS, $SnCl_4$, MeCN, rt, 17 h	 (37)	566
		TCS, HMDS, $SnCl_4$, MeCN, rt, 16 h	 (26)	566
		BSA, $SnCl_4$, MeCN, rt, 0.8 h	 (76) α:β = 2:3	569

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

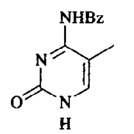
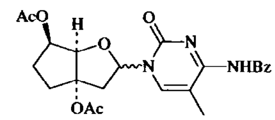
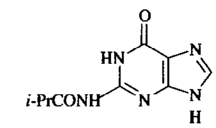
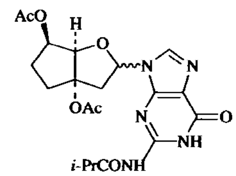
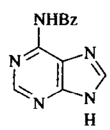
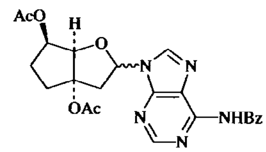
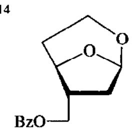
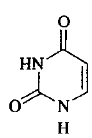
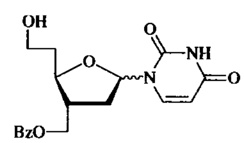
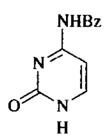
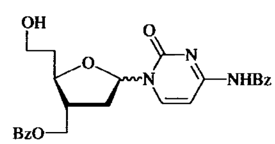
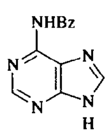
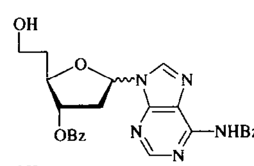
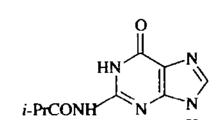
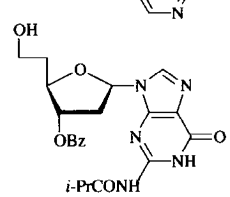
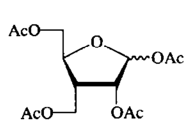
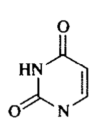
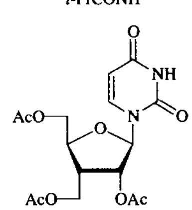
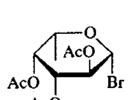
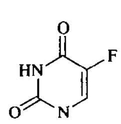
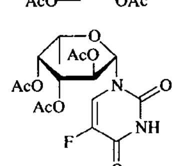
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TCS, HMDS, $SnCl_4$, MeCN, 0-55°, 70 min	 (76) α:β = 2:3	569
		BSA, TMSOTf, MeCN 1. rt, 60 h 2. 40°, 6 h	 (45) α:β = 8:5 + N^7-isomer (37) α:β = 3:2	569
		BSA, TMSOTf, MeCN 1. 80°, 2 h 2. rt, 3 h	 (78) α:β = 3:2	569
C_{14} 		BSA, TMSOTf, MeCN, rt, 15 min	 (75) α:β = 1:1	570
		BSA, TMSOTf, MeCN, 40°, 1 h	 (64) α:β = 1:1	570
		BSA, TMSOTf, MeCN, 40°, 30 min	 (64) α:β = 1:1	570
		BSA, TMSOTf, MeCN, 40°, 1 h	 (56) α:β = 1:1 + N^7-isomer (30)	570
		TCS, HMDS, $SnCl_4$, MeCN, rt, 2 h	 (41)	571
		HMDS, $Cl(CH_2)_2Cl$, $SnCl_4$, rt, 12 h	 (70)	367

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

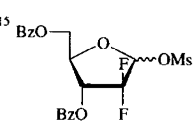
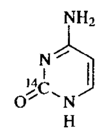
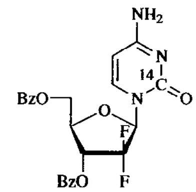
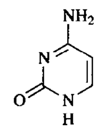
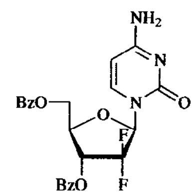
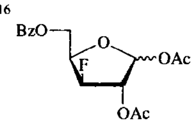
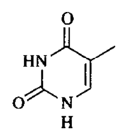
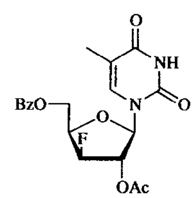
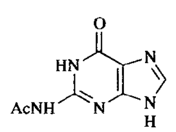
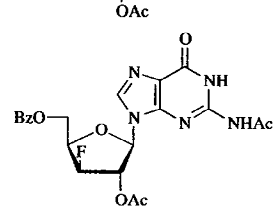
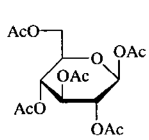
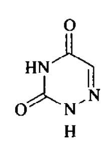
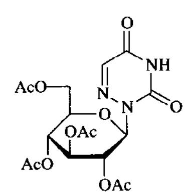
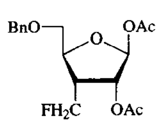
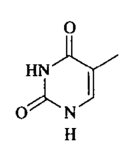
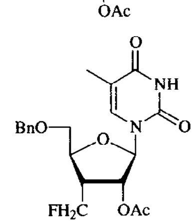
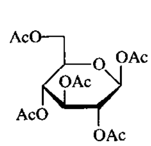
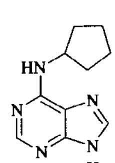
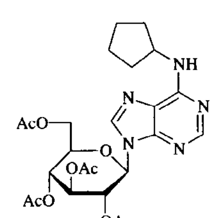
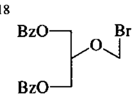
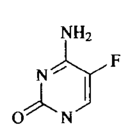
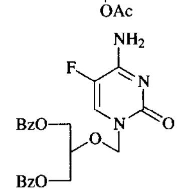
	Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			TCS, HMDS, TMSOTf, $Cl(CH_2)_2Cl$, reflux, 48 h	 (16)	572
			TCS, HMDS, TMSOTf, $Cl(CH_2)_2Cl$, reflux, 48 h	 (16)	572
C_{16}			BSA, TMSOTf, $Cl(CH_2)_2Cl$, MeCN, reflux 2 h	 (63)	564
			1. BSA, TMSOTf, MeCN, reflux 1 h 2. $NH_2NH_2{\bullet}H_2O$, Py/AcOH (1:4) rt, 5 h	 (58) + N^7-isomer (19)	573
			TCS, HMDS, $SnCl_4$, MeCN, 24°, 7 h	 (42)	189
C_{17}			TCS, HMDS, $C_4F_9SO_3K$, MeCN, reflux, 24 h	 (84)	574
			TCS, HMDS, TMSOTf, dioxane, rt, 12 h	 (35)	567
C_{18}			TCS, HMDS, $C_4F_9SO_3K$, MeCN, heat, 6 h	 (56)	575

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS *(Continued)*

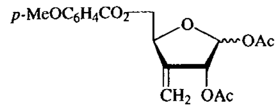
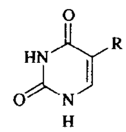
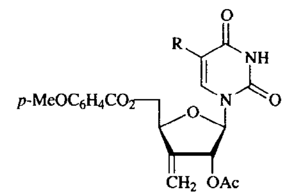
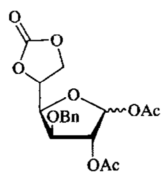
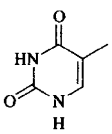
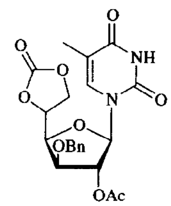
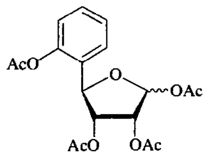
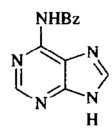
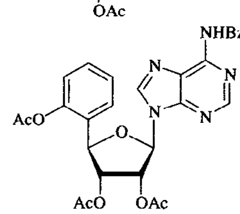
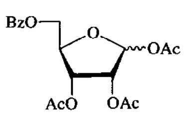
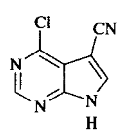
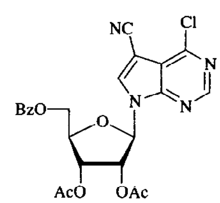
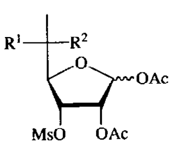
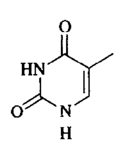
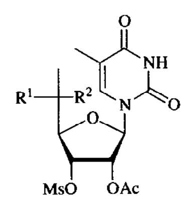
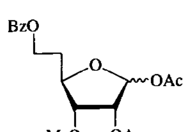
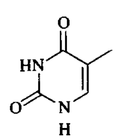
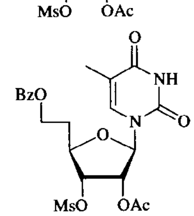
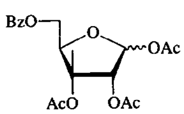
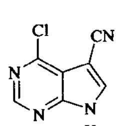
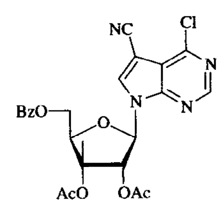
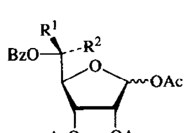
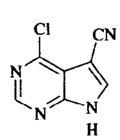
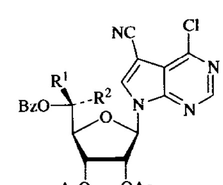
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TCS, HMDS, TMSOTf, $Cl(CH_2)_2Cl$, 60°, 2 h	 R: H (70); Me (47)	576, 577
		BSA, $SnCl_4$, $Cl(CH_2)_2Cl$ 1. 5°, 30 min 2. rt 30 min 3. reflux, 30 min	 (87)	578
		1. HMDS, TMSOTf, MeCN, 60°, 1 h 2. MeOH, NH_3, rt, 48 h	 (65)	579
		TCS, HMDS, TMSOTf, MeCN, heat, 20-24 h	 (31)	580
		TCS, HMDS, CF_3SO_3H, MeCN, rt, time	 R^1 / R^2 / time: BzO / H / 10 h (68); H / BzO / 7 h (53)	581
		TCS, HMDS, CF_3SO_3H, MeCN, rt, 4 h, or 80°, 5 h	 (46)	581-583
C_{19}				
		TCS, HMDS, TMSOTf, MeCN, heat, 20-24 h	 (28)	580
		TCS, HMDS, TMSOTf, MeCN, heat, 20-24 h	 R^1 / R^2: H / Me (47); Me / H (32)	580

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

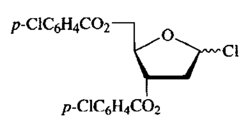
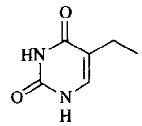
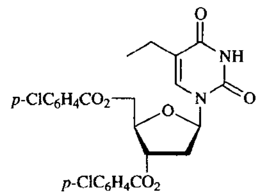
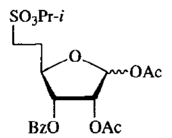
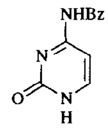
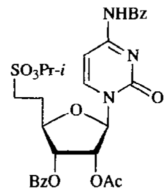
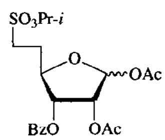
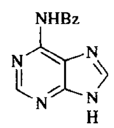
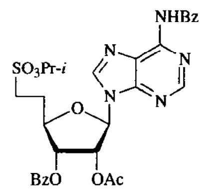
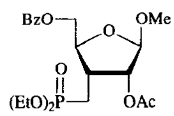
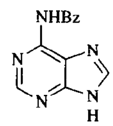
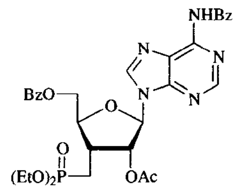
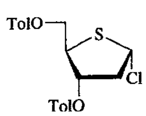
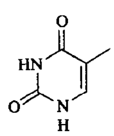
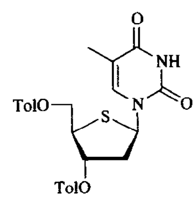
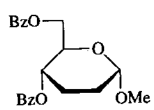
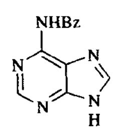
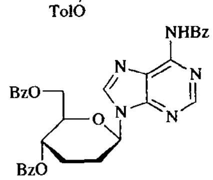
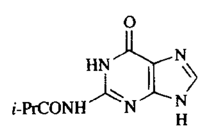
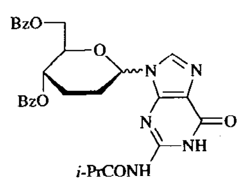
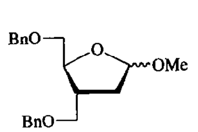
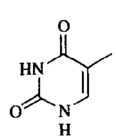
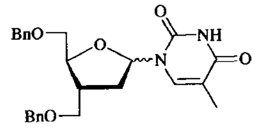
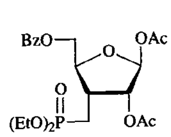
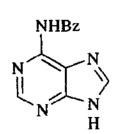
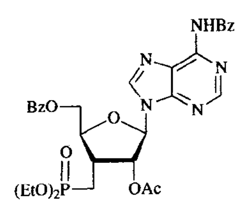
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TCS, HMDS, $SnCl_4$, MeCN	 (46) + α-anomer	584
C_{20}				
		HMDS, Py, $SnCl_4$, $Cl(CH_2)_2Cl$, 0°, 20 h	 (76)	508
		HMDS, Py, TMSOTf, $Cl(CH_2)_2Cl$, 40°, 20 h	 (51)	508
		TCS, HMDS, CF_3SO_3K, MeCN	 (60)	585
C_{21}				
		TCS, HMDS, TMSOTf, $Cl(CH_2)_2Cl$, −78°, 1.5 h	 (—)	586
		TCS, HMDS, $SnCl_4$, MeCN, rt, 20 h	 (35)	192
		BSA, TMSOTf, MeCN, 80°, 16 h	 (40) N^7:N^9 = 1:4	192
		"Vorbrüggen conditions"	 (—)	587
		TCS, HMDS, $C_4F_9SO_3K$, MeCN, reflux, 10 h	 (61)	588

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

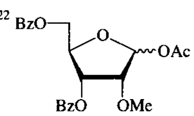
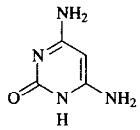
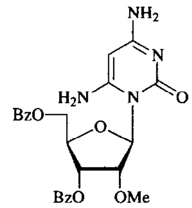
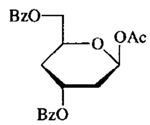
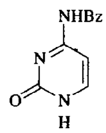
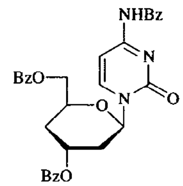
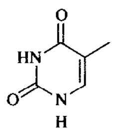
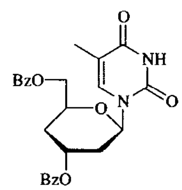
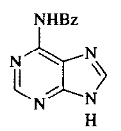
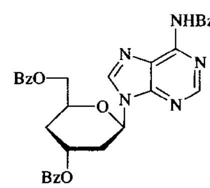
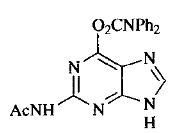
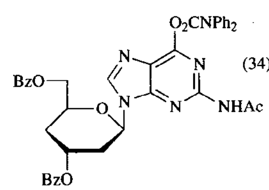
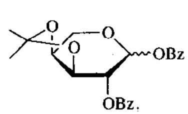
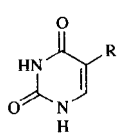
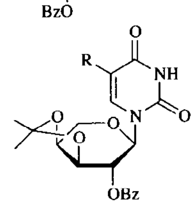
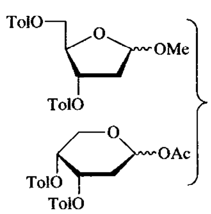
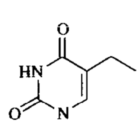
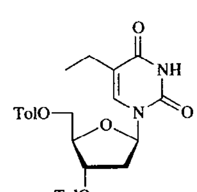
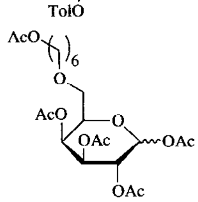
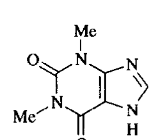
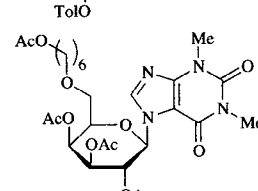
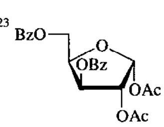
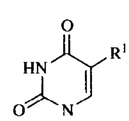
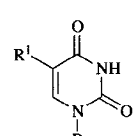
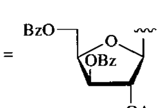
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 		BSA, TMSOTf, MeCN, 70°	 (67) + α-anomer (8)	589
		BSA, TMSOTf, $Cl(CH_2)_2Cl$, 70°	 (56) + α-anomer (8)	590
		BSA, TMSOTf, $Cl(CH_2)_2Cl$, Cond.	 Cond. / α-anomer: rt, 16 h (71) (9); 0°, 1 h, rt, 5 h (55) (22)	590
		BSA, TMSOTf, MeCN, 50°, 64 h	 (30)	590
		BSA, TMSOTf, $Cl(CH_2)_2Cl$, 50°, 64 h	 (34) + α-anomer (7)	590
		TCS, HMDS, $SnCl_4$, MeCN	 R: H (68); Me (70)	192h
		TCS, HMDS, $C_4F_9SO_3K$, MeCN, heat, 12 h	 (26) + α-anomer (21)	189
		TCS, HMDS, $SnCl_4$, MeCN, 80°, 4 h	 (56)	592
C_{23} 		TCS, HMDS, $SnCl_4$, MeCN, rt, 21 h	 I R^1 = H (82) R = 	192e

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

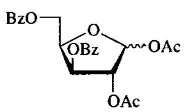
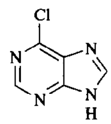
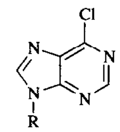
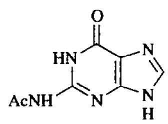
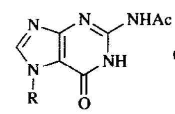
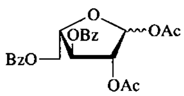
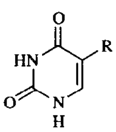
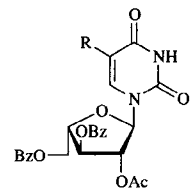
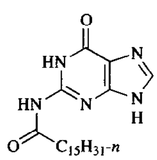
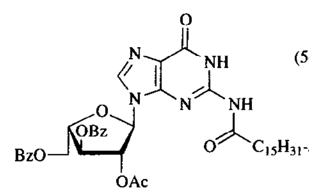
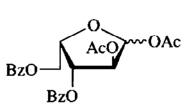
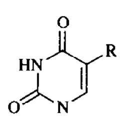
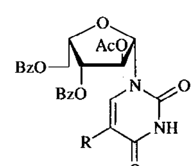
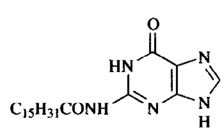
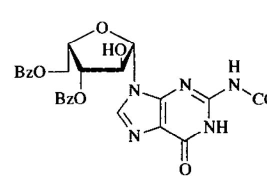
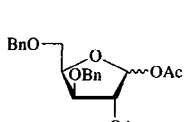
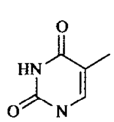
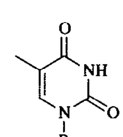
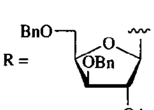
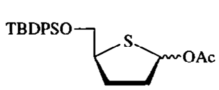
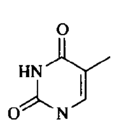
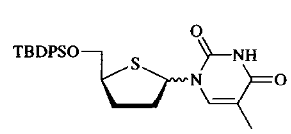
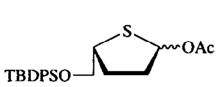
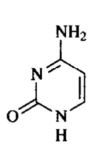
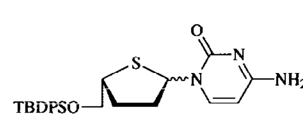
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TCS, HMDS, $SnCl_4$, MeCN	**I**, R^1 = H (82)	192f
		TCS, BSA, $SnCl_4$, MeCN, reflux, 5 min	**I**, R^1 = Me (46)	593
		TCS, HMDS, $SnCl_4$, MeCN, rt, 1 h	 (54) + N^7 isomer (20)	594
		BSA, TMSOTf, MeCN, reflux, 6 h	 (9) + N^9 isomer (59)	537
		TCS, HMDS, $SnCl_4$ Cond.	 R / Cond. / / N^7-isomer H / rt, 60° / (69) / (11) Me / MeCN / (—) / (—) Me / reflux, 1.5 h / (64) / (—)	595 596 595
		1. BSA, TMSOTf, MeCN, reflux, 6 h 2. $NH_2NH_2 \cdot H_2O$, rt, 7 h	 (54) + N^7-isomer (16)	595
		TCS, HMDS, $SnCl_4$, MeCN, rt, 24 h	 R H (66) Me (64)	596
		1. BSA, TMSOTf, MeCN, reflux, 6 h 2. $H_2NNH_2 \cdot H_2O$, Py, AcOH, rt, 3 h	 (54) + N^7-isomer (16)	595
		TCS, HMDS, $SnCl_4$, MeCN, reflux, 0.5 h	 (70) R = 	598, 599
		TCS, HMDS, $C_4F_9SO_3K$, MeCN, rt, 12 h	 (90) α:β = 4:3	600
		TCS, HMDS, $C_4F_9SO_3K$, MeCN, 25°, 12 h	 (68) 1:1	597

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

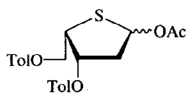
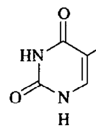
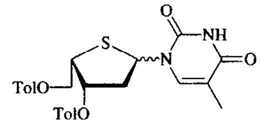
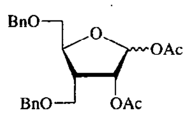
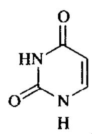
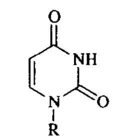
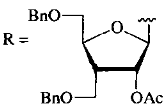
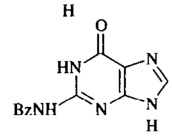
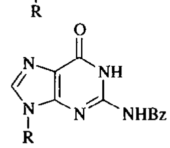
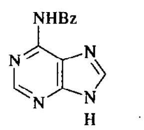
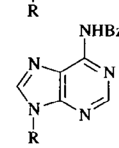
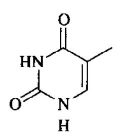
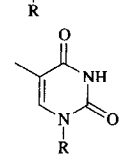
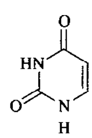
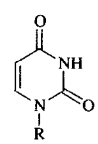
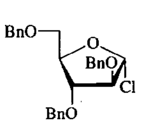
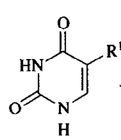
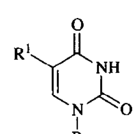
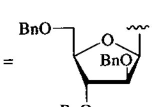
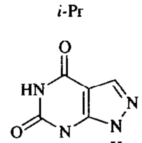
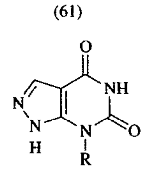
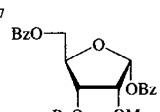
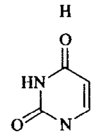
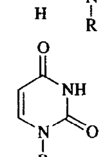
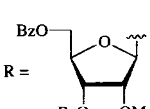
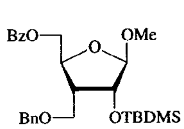
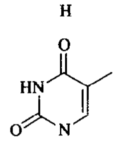
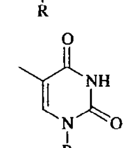
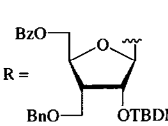
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TCS, HMDS, TMSOTf, MeCN, –78°, 1.5 h	 (—)	601
C_{24} 		TCS, HMDS, $C_4F_9SO_3K$, MeCN	 (—) R = 	587
		TCS, HMDS, $C_4F_9SO_3K$, MeCN	 (—)	587
		TCS, HMDS, $C_4F_9SO_3K$, MeCN	 (—)	587
		TCS, HMDS, $SnCl_4$, MeCN, rt, 4 h	 (91)	571
		TCS, HMDS, CF_3SO_3H, MeCN 1. rt, 3.5 h 2. 60°, 40 min	 I (78)	571
		TCS, HMDS, $SnCl_4$, MeCN, rt, 4 h	I (79)	571
		TCS, HMDS, CF_3SO_3K, MeCN, reflux	I (87) + α-anomer (6)	574
C_{26} 		TCS, HMDS, $SnCl_4$, MeCN	 R = 	
	R^1			
	Et	—	(—)	602
	n-Pr	—	(—)	602
	n-Bu	—	(—)	602
	CH=CH$_2$	—	(65)	602
	CH=CH$_2$	or $Cl(CH_2)_2Cl$	(65)	363
	i-Pr	rt, 24 h	(61)	359
		TCS, HMDS, TMSOTf, $Cl(CH_2)_2Cl$, rt, 10 h	 (33) + N^7-isomer (2)	361
C_{27} 		HMDS, $(NH_4)_2SO_4$, $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 1 h	 (74) R = 	226
		BSA, $SnCl_4$, MeCN, 80°, 11 h	 (73) α:β = 1:1 R = 	226a

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

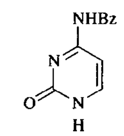
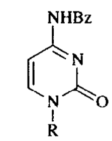
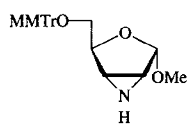
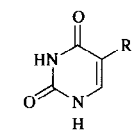
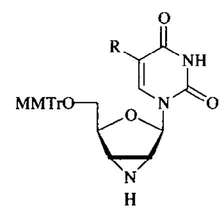
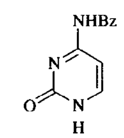
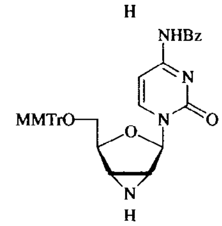
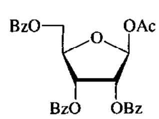
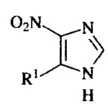
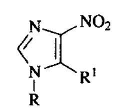
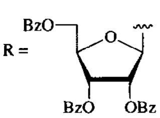
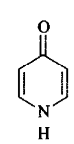
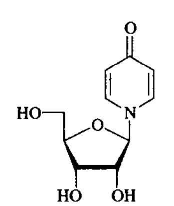
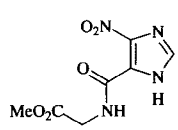
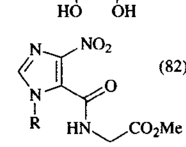
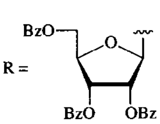
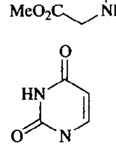
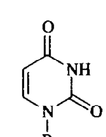
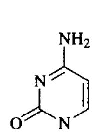
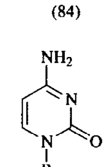
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		HMDS, $(NH_4)_2SO_4$, $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 1 h	 (70)	226
C_{28} 		TCS, HMDS, TBDMSOTf, MeCN, 124°	 R: H (20); Me (20)	232
		TCS, HMDS, TMSOTf, MeCN, 124°	 (20)	232
		TCS, HMDS, $SnCl_4$, MeCN, rt	 R = 	
	R^1			
	Cl	2 h	(77)	603
	CO_2H	0.5 h	(>90)	604
	Br	2 h	(85)	603
	I	2 h	(61)	603
		1. TCS, HMDS, $C_4F_9SO_3K$, MeCN, heat, 24 h 2. NH_3, MeOH	 (50)	189
		TCS, HMDS, CF_3SO_3H, MeCN, rt, 0.5 h	 (82) R = 	604
		TCS, HMDS, MeCN		
		$SnCl_4$, rt, 2 h	(83)	189
		NaI	(66)	137
		$NaBF_4$, 83°, 2 h	(42)	188
		NH_4ClO_4, 83°, 19 h	(40)	188
		$NH_4ClO_4{\cdot}H_2O$, 83°, 19 h	(58)	188
		CF_3SO_3H, rt, 4 h, reflux 0.5 h	(81)	189
		$C_4F_9SO_3K$, heat	(84)	189
		TCS, HMDS, $C_4F_9SO_3K$, MeCN, heat, 26 h	 (56)	189

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

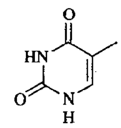
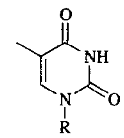
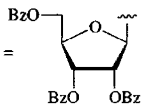
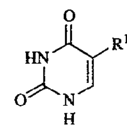
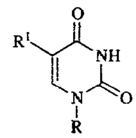
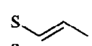
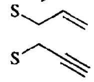
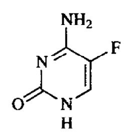
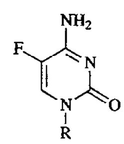
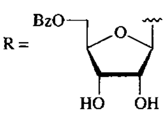
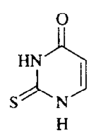
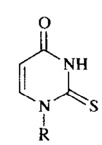
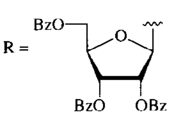
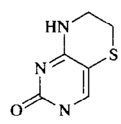
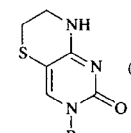
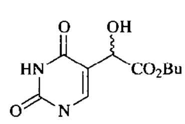
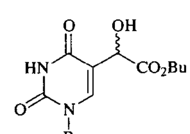
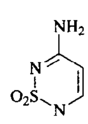
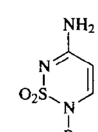
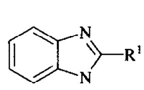
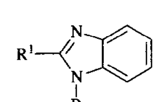
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TCS, HMDS, CF_3SO_3H, MeCN, rt, 4 h	 (88) R = 	605, 606
		TCS, HMDS, MeCN		
	R^1			
	Me	$SnCl_4$	(—)	586
	Me	CF_3SO_3H, heat, 1 h	(88)	607
	Me	TMSOTf, reflux, 0.5 h	(82)	606
	OMe	$C_4F_9SO_3K$, reflux, 20 h	(70)	189, 608, 609
	SMe	$C_4F_9SO_3K$, reflux, 20 h	(48)	610
		$C_4F_9SO_3K$, reflux, 20 h	(70)	610
		$C_4F_9SO_3K$, reflux, 20 h	(72)	610
				610
		$C_4F_9SO_3K$, reflux, 20 h	(48)	610
	SBn	$C_4F_9SO_3K$, reflux, 20 h	(51)	
		1. TCS, HMDS, MeCN, $C_4F_9SO_3K$, reflux, 24 h 2. Amberlyst A-26, MeOH	 (55) R = 	534
		TCS, HMDS, $SnCl_4$, MeCN, rt, 6.5 h	 (59) R = 	189
		HMDS, TMSOTf, MeCN	 (28)	610
		TCS, HMDS, CF_3SO_3H	 (76%) 1:1 mixture	611
		TCS, HMDS, $C_4F_9SO_3K$, MeCN, heat, 24 h	 (41)	191
		TCS, HMDS, CF_3SO_3H, MeCN		612
	R^1			
	H		(—)	
	CF_3		(—)	
	CH_2CN		(—)	
	Bn		(—)	
	SCF_3		(—)	
	CH_2SCF_3		(—)	

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

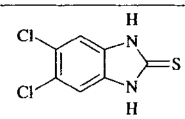
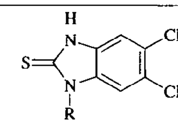
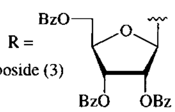
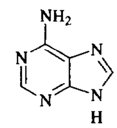
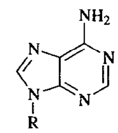
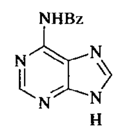
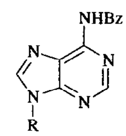
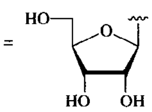
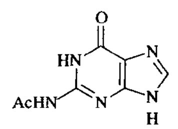
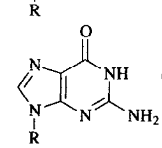
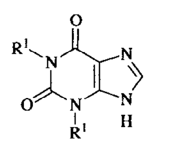
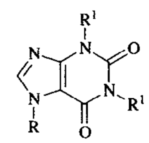
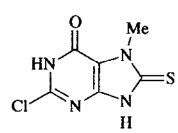
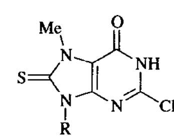
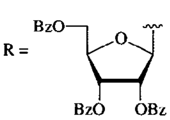
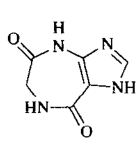
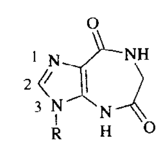
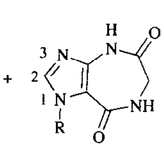
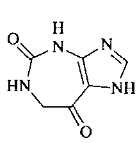
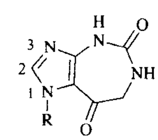
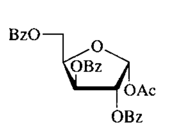
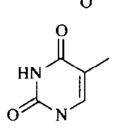
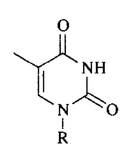
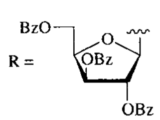
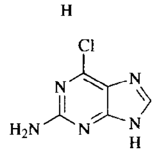
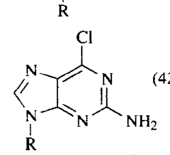
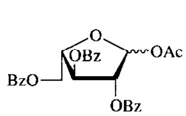
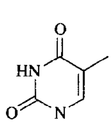
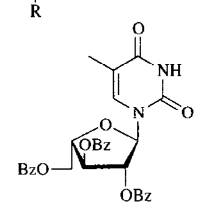
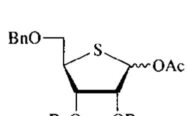
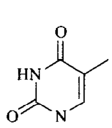
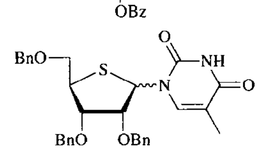
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		BSA, TMSOTf, MeCN, reflux, 18 h	 (74) R =  + *N,N*-bisriboside (3)	613
		TCS, HMDS, $C_4F_9SO_3K$, MeCN	 (62)	614
		1. TCS, HMDS, $C_4F_9SO_3K$, MeCN, heat, 21 h 2. NH_3, MeOH	 (63) R = 	189
		1. TCS, HMDS, $C_4F_9SO_3K$, MeCN, heat, 21 h 2. NH_3, MeOH	 (44)	189
		1. TCS, HMDS, $C_4F_9SO_3K$, MeCN, reflux, 30 min 2. NH_3, MeOH, rt, 2 days	 R^1: Me (—); *n*-Pr (—); *n*-Bu (—)	615
		TCS, HMDS, TMSOTf, MeCN, reflux, 3.5 h	 (76) R = 	616
		TCS, HMDS, CF_3SO_3H, MeCN rt, 17 h	 (14) +  (51)	617
		TCS, HMDS, CF_3SO_3H, MeCN rt, 1 h	 (35) + isomer (15)	618
		TCS, HMDS, $SnCl_4$, MeCN, reflux, 20 min	 (72) R = 	192e
		TCS, HMDS, $SnCl_4$, MeCN, reflux, 20 min	 (42) + N^7-isomer (34)	192e
		TCS, HMDS, $SnCl_4$, MeCN, reflux, 1 h	 (60)	619
		TCS, HMDS, $SnCl_4$, MeCN, reflux, 20 min	 (39)	620

TABLE I. ONE STEP-ONE POT SILYLATION/COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS *(Continued)*

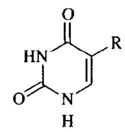
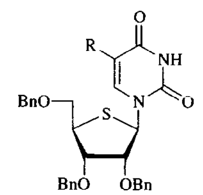
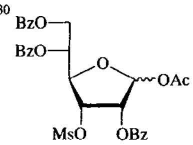
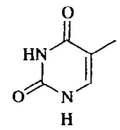
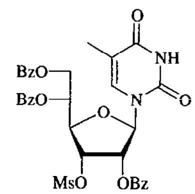
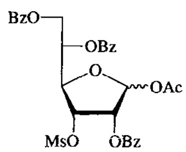
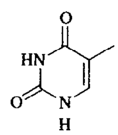
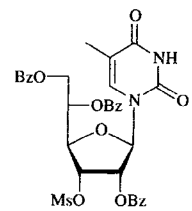
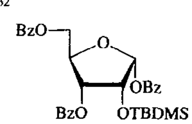
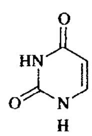
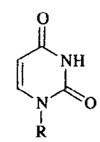
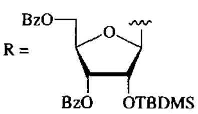
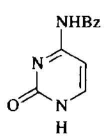
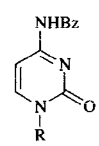
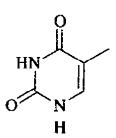
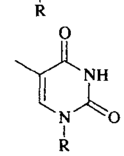
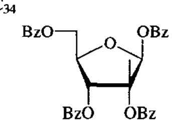
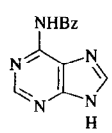
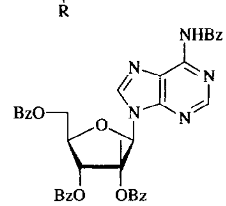
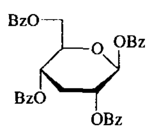
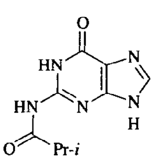
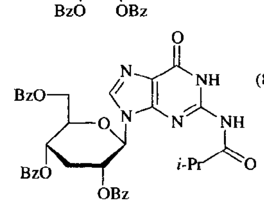
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		BSA, TMSOTf, MeCN, rt, 2.5 h	 R / H (42) α-anomer (31) / Me (41) α-anomer (37)	620
C_{30} 		TCS, HMDS, TMSOTf, MeCN, rt, 12 h	 (69)	581
		TCS, HMDS, TMSOTf, MeCN, rt, 8 h	 (69)	581
C_{32} 		HMDS, $(NH_4)_2SO_4$, $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 1 h	 (95) R = 	226
		HMDS, $(NH_4)_2SO_4$, $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 1 h	 (86)	226
		TCS, HMDS, $SnCl_4$, MeCN, reflux, 20 min	 (87)	621, 226
C_{34} 		BSA, TMSOTf, MeCN, 80°, 3 h	 (86)	622, 623
		BSA, TMSOTf, MeCN, 80°, 16 h	 (89) β-N^9:β-N^7 = 3:2	192

TABLE II. ONE STEP-ONE POT COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS

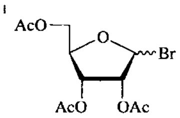
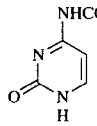
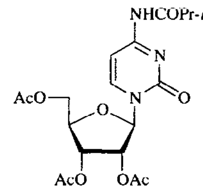
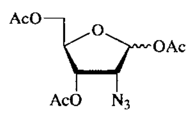
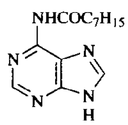
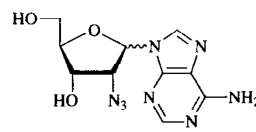
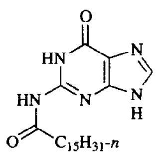
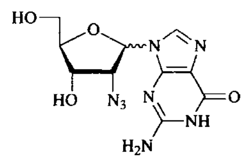
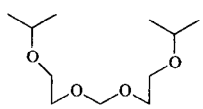
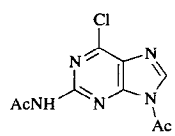
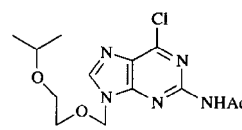
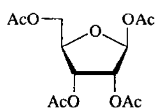
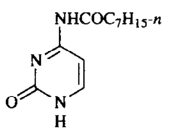
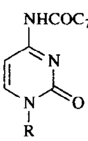
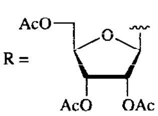
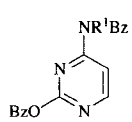
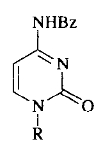
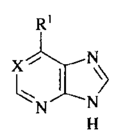
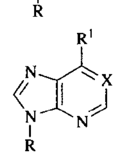
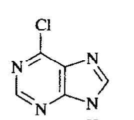
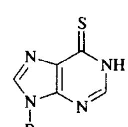
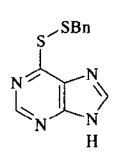
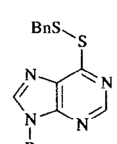
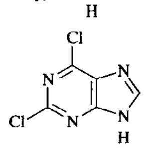
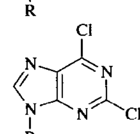
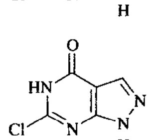
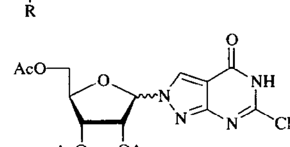
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		$SnCl_4$, $Cl(CH_2)_2Cl$, 50°, 3 h	 (50)	424a
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 15 h 2. NaOMe	 (60-65) $\alpha:\beta$ = 1:2	624
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 90 min 2. NaOMe, MeOH, 37°, 12 h	 (42) $\alpha:\beta$ = 1.2:3 + N^9-isomer (58), $\alpha:\beta$ = 0.7:5.1	624
		TMSOTf, HMDS, $Cl(CH_2)_2Cl$, –30°	 (58)	521
C_{13} 		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 (80) R = 	180
		$SnCl_4$, $Cl(CH_2)_2Cl$	 R^1: H 0°, 5 min, rt, 12 h (83) Bz 0°, 20 min, rt, 2 h (59)	424
		$SnCl_4$, MeCN, rt	 R^1 / X H CH 5 h (57) NO_2 CH 7 h (82) NH_2 N (—) (100) NH_2 N 12 h (77) SMe N 12 h (—)	625 626 625 192a 192a
		1. $SnCl_4$, MeCN, rt, 12 h 2. thiourea, EtOH, reflux 3. rt, 12 h	 (78)	192a
		1. $SnCl_4$, MeCN, rt, 12 h 2. $HS(CH_2)_2OH$, EtOH, rt, 3 h	 (85)	192a
		$SnCl_4$, MeCN, rt, 12 h	 (81)	192a
		$SnCl_4$, MeCN, rt, 16 h	 (50)	627

TABLE II. ONE STEP-ONE POT COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

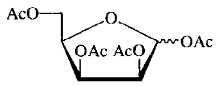
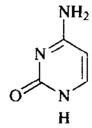
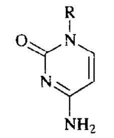
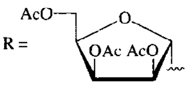
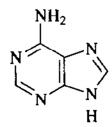
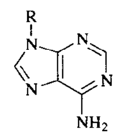
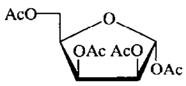
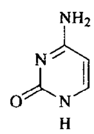
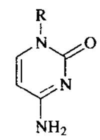
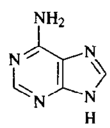
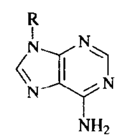
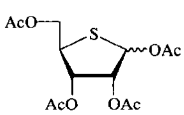
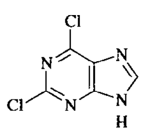
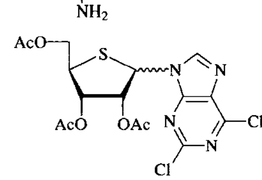
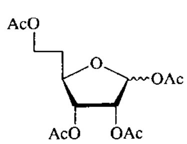
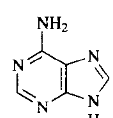
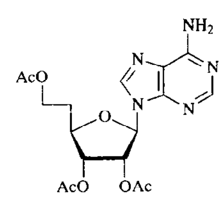
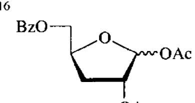
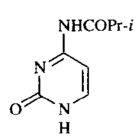
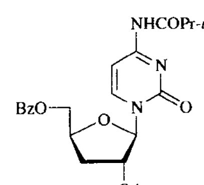
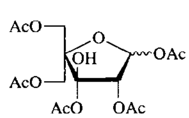
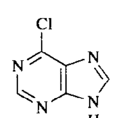
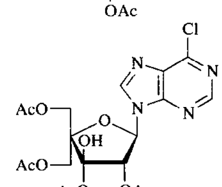
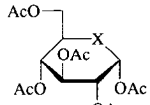
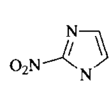
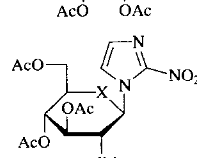
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, rt, 23 h	 (—) R = 	537
		$SnCl_4$, MeCN, rt, 23 h	 (—)	537
		$SnCl_4$, MeCN	 (31)	192f
		$SnCl_4$, MeCN	 (100)	192f
		$SnCl_4$, MeCN or CH_2Cl_2, rt, 12 h	 (70) α:β = 1:3	86a
C_{14} 		$SnCl_4$, MeCN	 (70)	628
C_{16} 		$SnCl_4$, $Cl(CH_2)_2Cl$, 27°, 20 h	 (62)	192o
		$SnCl_4$, $Hg(CN)_2$, MeCN, 55°, 2 h	 (84)	629
		$SnCl_4$, $Hg(CN)_2$, MeCN, 1.5 h	 X: O 60° (61); S 60-70° (24)	630, 630

TABLE II. ONE STEP-ONE POT COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

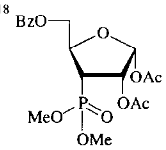
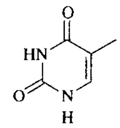
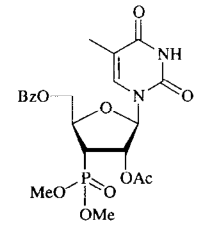
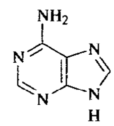
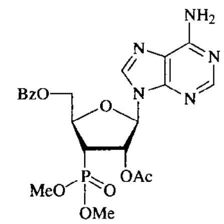
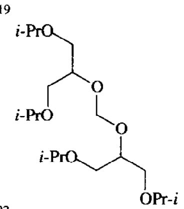
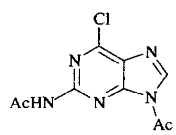
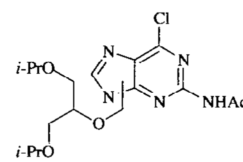
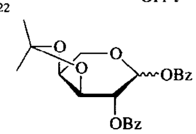
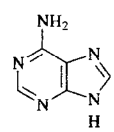
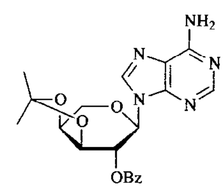
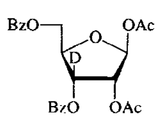
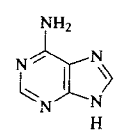
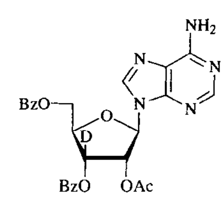
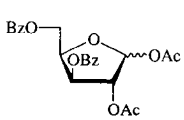
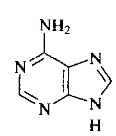
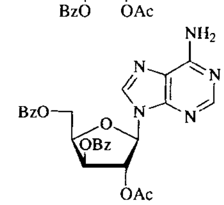
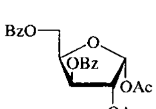
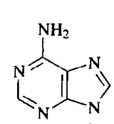
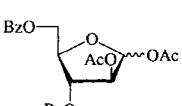
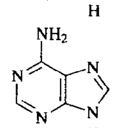
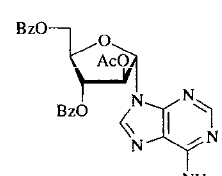
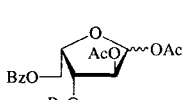
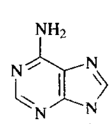
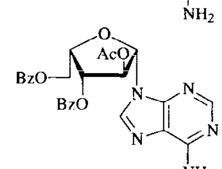
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 		$SnCl_4$, MeCN, rt, 5 d	 (29)	192j
		$SnCl_4$, MeCN, rt, 5 d	 (28)	192j
C_{19} 		$SnCl_4$, 100°, 8 h	 DMF (64) N^9:N^7 = 93.2:2.5 NMP (75) —	521
C_{22} 		$SnCl_4$, MeCN	 (74)	192h
C_{23} 		$SnCl_4$, MeCN, rt	 (75)	192d
		$SnCl_4$, MeCN, rt, 15 h	 I (70)	192f
		$SnCl_4$, MeCN, rt, 15 h $SnCl_4$, MeCN	I (70) I (70)	192e
		$SnCl_4$, MeCN, rt, 18 h	 (66)	595
		$SnCl_4$, MeCN, rt, 20 h	 (61)	192i

TABLE II. ONE STEP-ONE POT COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

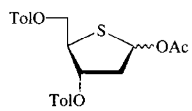
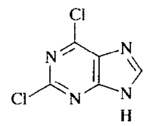
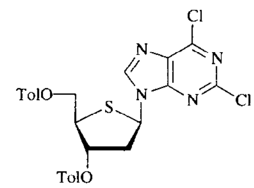
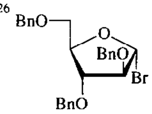
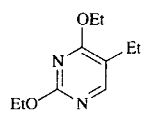
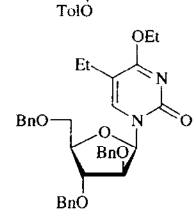
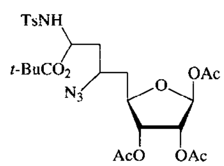
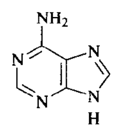
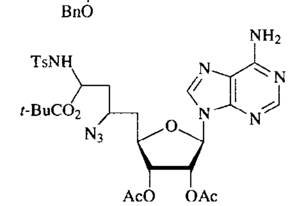
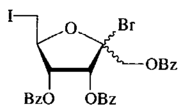
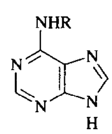
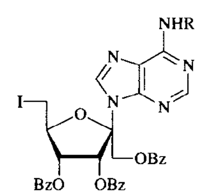
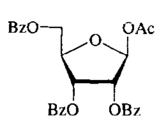
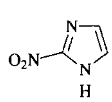
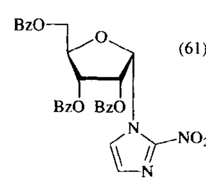
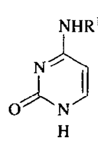
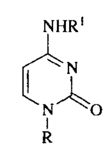
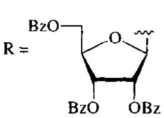
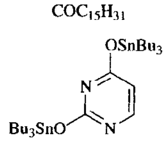
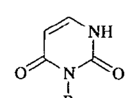
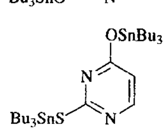
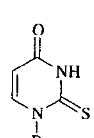
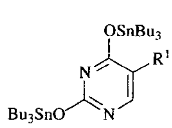
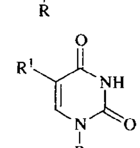
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, 0°, 1.5 h	 (71)	631
C_{26} 		$SnCl_4$, MeCN, rt, 6 d	 (49)	358
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 16 h	 (59)	192g, 86h
C_{27} 		$SnCl_4$, $Hg(CN)_2$, MeCN, 60°, 2 h	 R: H (21), α-anomer (7); COC_5H_{11}-*n* (46), α-anomer (12)	632
C_{28} 		$SnCl_4$, $Hg(CN)_2$, MeCN, 60°, 75 min	 (61)	213
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 20 h	 R = 	180
	R^1 = COPr-*i*		(64)	
	COC_7H_{15}		(80)	
	COCH(Et)Bu		(72)	
	$COC_{15}H_{31}$		(81)	
		$SnCl_4$, CH_2Cl_2, 10°, 6 d	 (60) + N^1-isomer (40)	426
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 19 h	 (90)	426
		$SnCl_4$, $Cl(CH_2)_2Cl$	 R = Br, rt, 12 h (97)	426
			Me, 20°, 2 d (63)	426

TABLE II. ONE STEP-ONE POT COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

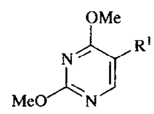
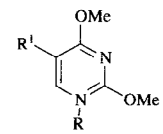
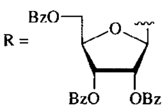
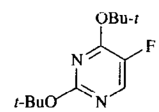
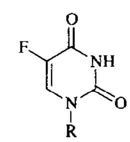
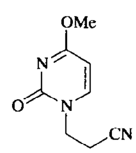
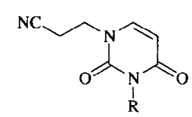
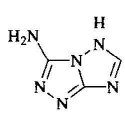
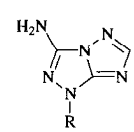
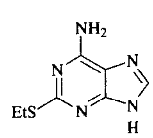
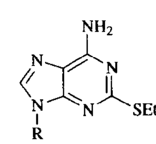
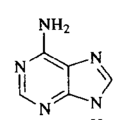
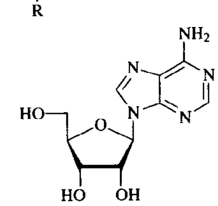
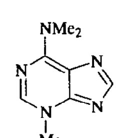
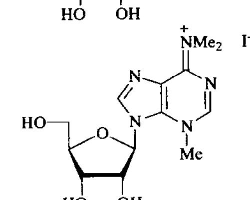
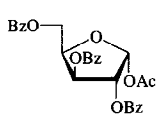
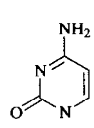
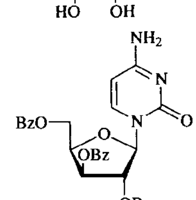
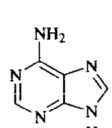
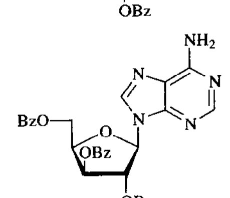
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN	 R = 	
	R^1			
	F	50-60°, 10 h	(87)	514b
	Me	rt, 12 h	(99)	633
	Et	rt, 12 h	(92)	633
	Pr-*n*	rt, 12 h	(90)	633
	Bu-*n*	rt, 12 h	(94)	633
	C_5H_{11}-*n*	rt, 12 h	(95)	633
	C_6H_{13}-*n*	rt, 12 h	(99)	633
		$SnCl_4$, MeCN, rt, 30 min	 (97)	634
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (21)	254
		$SnCl_4$, MeCN, rt, 24 h	 (7) + N^1-α-isomer (—) + N^2-β-isomer (30)	635
		$SnCl_4$, $MeNO_2$, rt, 18 h	 (63)	591
		1. $SnCl_4$, MeCN, rt, 24 h 2. NH_3, MeOH	 (78)	192a
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt 2. NaI	 (35)	636
		$SnCl_4$, MeCN, rt, 15 h	 (33)	192e, 192i
		$SnCl_4$, MeCN, rt, 30 min	 (68)	192b

TABLE II. ONE STEP-ONE POT COUPLING OF HETEROCYCLIC BASES WITH SUGARS - FRIEDEL-CRAFTS CATALYSTS (*Continued*)

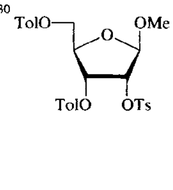
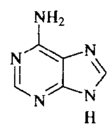
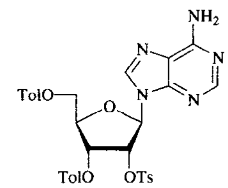
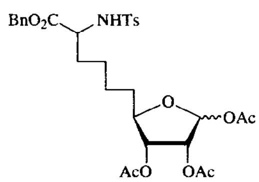
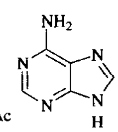
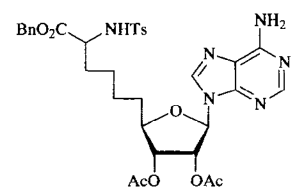
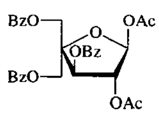
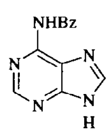
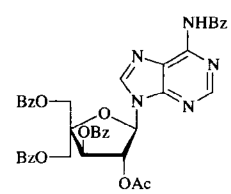
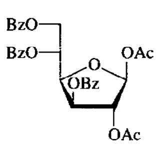
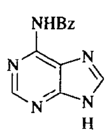
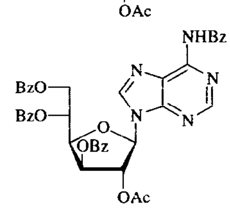
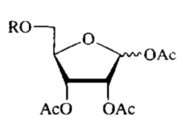
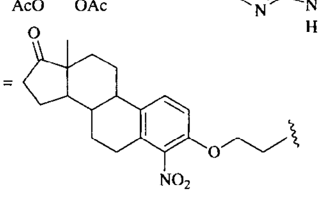
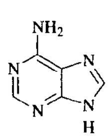
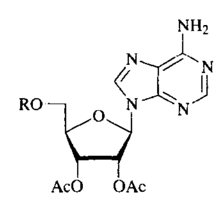
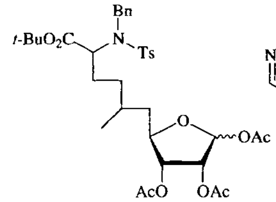
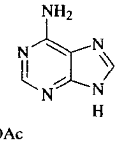
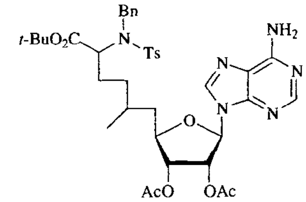
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{30} 		$SnCl_4$, MeCN	 (—)	213
		$SnCl_4$, MeCN, 22°, 4.5 h	 (61)	86b
C_{31} 		$SnCl_4$, MeCN, 24°, 18 h	 (73)	192n
		$SnCl_4$, MeCN, 24°, 18 h	 (79)	192n
 R = 		$SnCl_4$, MeCN, rt, 18 h	 (64)	192c
		$SnCl_4$, MeCN, rt, 17 h	 (67)	86b

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST

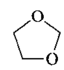
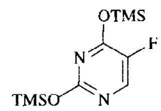
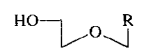
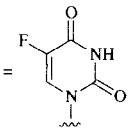
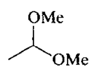
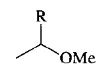
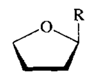
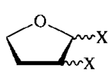
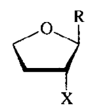
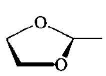
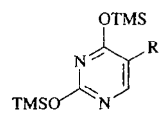
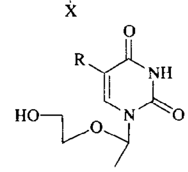
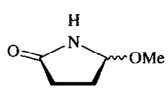
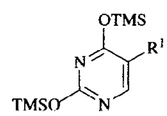
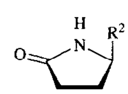
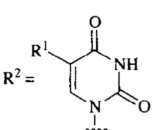
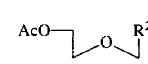
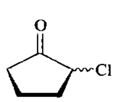
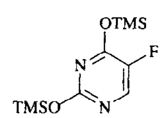
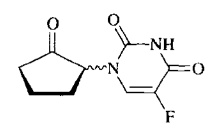
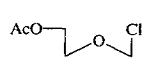
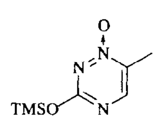
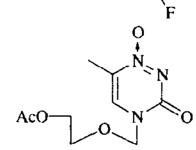
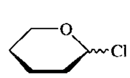
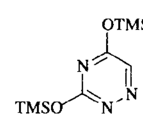
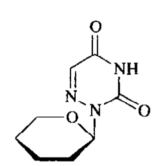
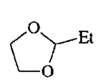
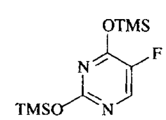
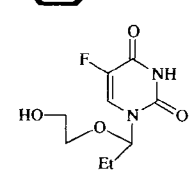
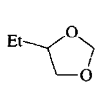
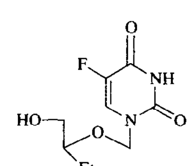
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		1. $SnCl_4$, CH_2Cl_2, rt, 1 h 2. $NaHCO_3$, MeOH, rt, 1 h	 (23) R = 	637
C_4 		$SnCl_4$, $CHCl_3$, rt, 20 min	 (62)	638
		1. H_2O 2. $SnCl_4$, dioxane, rt, 3 h	 I (26)	639
		1. H_2O 2. $SnCl_4$, PhMe, rt, 3 h	I (86)	639
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 X: Cl (51) + *cis* isomer (23); Br (51) + *cis* isomer (22)	640 640
		$SnCl_4$, CH_2Cl_2, rt, 1 h	 I R: H (65); F (33); Me (54)	641
		1. $SnCl_4$, $CHCl_3$, rt, 0.5 h 2. $NaHCO_3$, MeOH	I R = H (—)	637
C_5 		$SnCl_4$, CH_2Cl_2, MeCN, 0-5°, 6 h; rt, 6 h	 R^1 = F, (41) R^2 = 	642
		$SnCl_4$, CH_2Cl_2, rt, 48 h	 $R^1 = CF_3$, (55)	643
		$SnCl_4$, CH_2Cl_2 reflux, 12 h	 (10)	644
		$SnCl_4$, CH_2Cl_2, rt, 16 h	 (44)	645
		$SnCl_4$, CH_2Cl_2, MeCN, $Cl(CH_2)_2Cl$, 4°, 2 h	 (92)	84
		$SnCl_4$, CH_2Cl_2, rt, 1 h	 I (75)	641
		1. $SnCl_4$, $CHCl_3$, rt, 3 h 2. $NaHCO_3$, MeOH	I (—)	637
		1. $SnCl_4$, $CHCl_3$, rt, 3 h 2. $NaHCO_3$, MeOH	 (—)	637

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

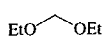
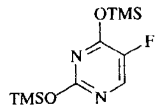
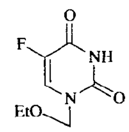
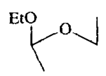
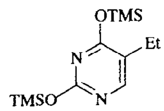
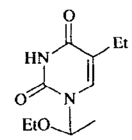
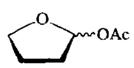
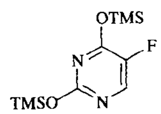
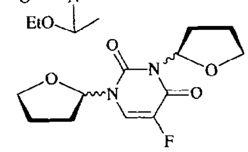
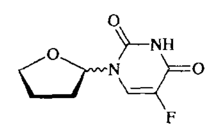
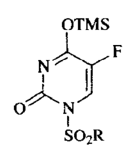
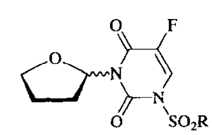
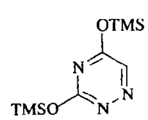
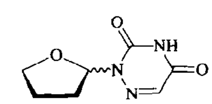
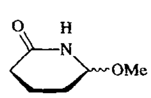
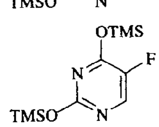
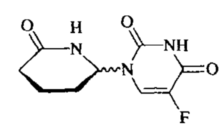
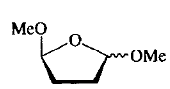
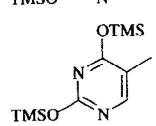
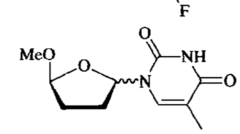
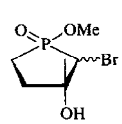
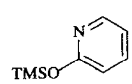
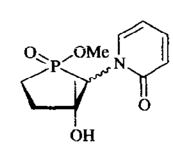
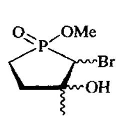
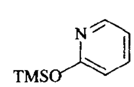
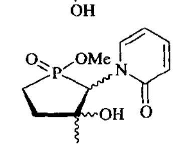
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $CHCl_3$, rt, 20 min	 (14) + N^3-isomer (15) + N^1,N^3-bis(isomer) (9)	638
C_6				
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 48 h	 (77)	646
		$SnCl_4$, CH_2Cl_2	 I (—)	647
		$SnCl_4$ (0.01 eq), CH_2Cl_2, rt, 3 h	I (96)	528
		$SnCl_4$	 I (82)	648
		$SnCl_4$ (0.1 eq), CH_2Cl_2, rt, 8 h	I (61)	528
		$SnCl_4$ (0.1 eq), CH_2Cl_2, rt, 1.5 h	I (81)	528
		$SnCl_4$ (0.01 eq), CH_2Cl_2, rt, 3 h	I (93)	528
		$SnCl_4$, CH_2Cl_2	 R: Me (72) Ph (62)	649 649
		$SnCl_4$	 (80)	648
		$SnCl_4$, CH_2Cl_2, MeCN, −20 to −25°, 6 h; rt, 6 h	 (40)	642
		$SnCl_4$, $Cl(CH_2)_2Cl$, −10°	 (75) *cis:trans* = 1:1	650
		$SnCl_4$, MeCN, $Cl(CH_2)_2Cl$, 80°, 24 h	 (28)	651
		$SnCl_4$, MeCN, reflux, 24 h	 I (28)	652
		$SnCl_4$, MeCN, $Cl(CH_2)_2Cl$, reflux, 24 h	I (4)	652
		$SnCl_4$, MeCN, DMF, reflux, 24 h	I (11)	652

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

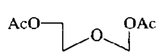
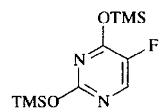
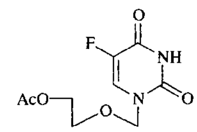
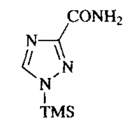
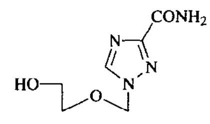
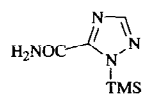
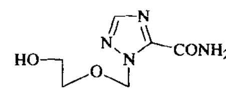
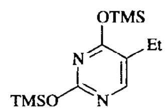
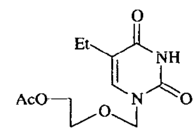
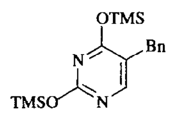
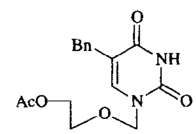
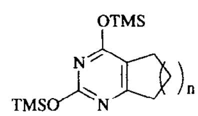
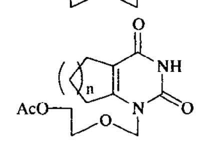
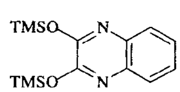
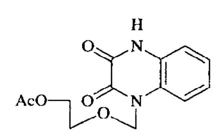
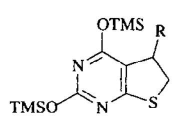
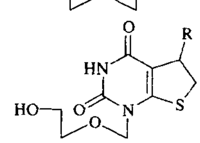
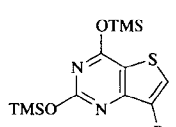
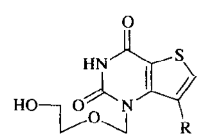
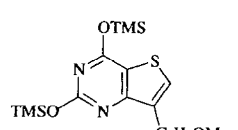
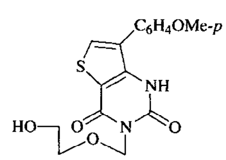
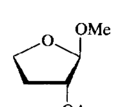
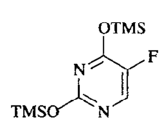
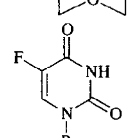
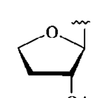
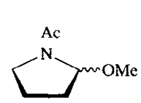
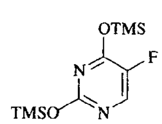
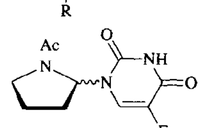
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$SnCl_4$, CH_2Cl_2, rt, 18 h	 (46)	643
		1. $SnCl_4$ 2. NH_3, MeOH	 (—)	653
		1. $SnCl_4$ 2. NH_3, MeOH	 (—)	653
		$SnCl_4$, MeCN, rt, 48 h	 (41)	654
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h	 (19) + N^3-isomer (9) + N^1,N^3-bis(isomer) (13)	655
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h	 n: 1 (40); 2 (74)	656
		$SnCl_4$, MeCN, rt, 48 h	 (18) + N^1,N^4-bis(isomer) (23)	657
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. NH_3, MeOH	 R: H (33); Ph (15)	658
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, −30°, 8 h 2. NH_3, MeOH	 R: p-FC_6H_4 (24); p-ClC_6H_4 (31); p-BrC_6H_4 (27); Me (62) + N^3-isomer (23); Ph (35); p-MeC_6H_4 (27)	659
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, −30°, 8 h 2. NH_3, MeOH	 (54) + N^1-isomer (48)	659
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (33) R = 	660
		$SnCl_4$, CH_2Cl_2, −13 to −15°, 3 h	 (81)	642

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

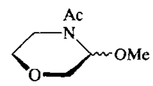
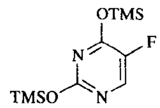
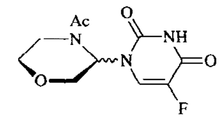
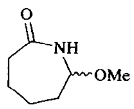
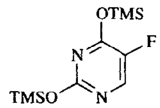
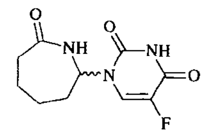
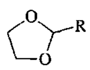
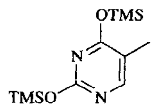
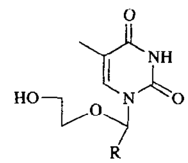
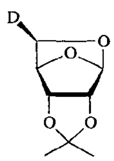
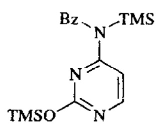
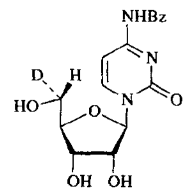
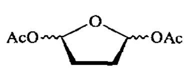
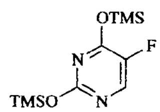
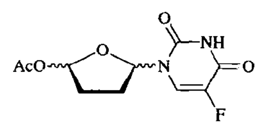
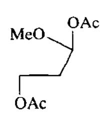
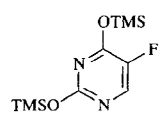
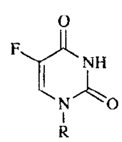
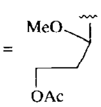
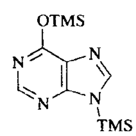
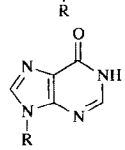
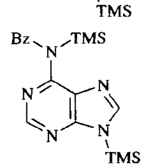
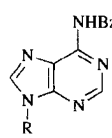
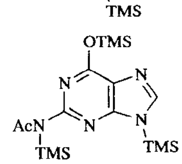
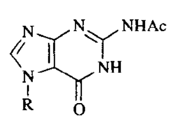
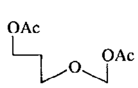
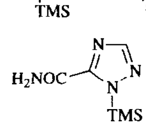
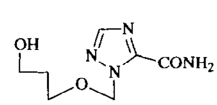
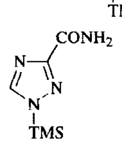
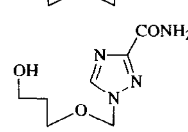
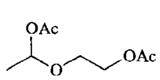
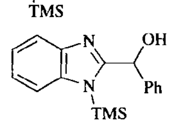
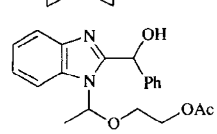
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, –20 to –25°, 24 h	 (60)	642
		$SnCl_4$, CH_2Cl_2, MeCN –20 to –25°, 6 h	 (36)	642
C_{7-8} 		$SnCl_4$, CH_2Cl_2, 20°, 2 d	 R: 2-furyl (48); 3-furyl (68); 2-pyridyl (48); 3-pyridyl (51)	661
C_8 		$SnCl_4$, MeCN	 (—)	662
		$SnCl_4$, CH_2Cl_2, rt, 4 h	 (65)	640
		$SnCl_4$, MeCN, –78°, 15 min; 25°, 4 h	 (47) R = 	663
		$SnCl_4$, MeCN, –78°, 15 min; 25°, 20 h	 (45) + N^7-isomer (—)	664
		$SnCl_4$, MeCN, –78°, 15 min; 25°, 20 h	 (81)	664
		$SnCl_4$, MeCN, –78°, 15 min; 25°, 20 h	 (21) + N^7-isomer (12)	664
		1. $SnCl_4$ 2. NH_3, MeOH	 (—)	653
		1. $SnCl_4$ 2. NH_3, MeOH	 (—)	653
		$SnCl_4$, MeCN, reflux	 (41)	665

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

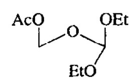
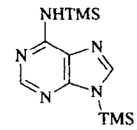
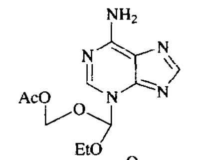
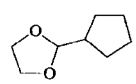
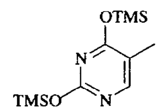
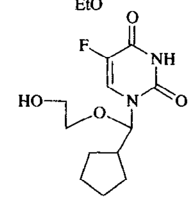
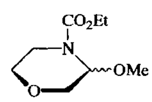
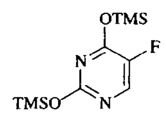
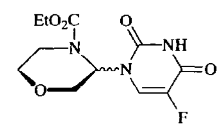
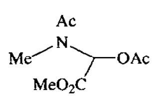
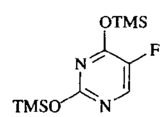
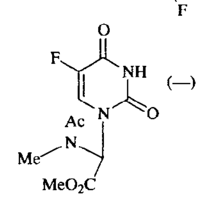
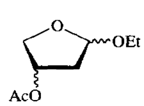
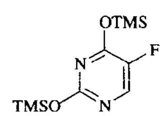
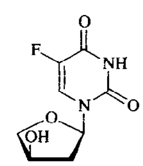
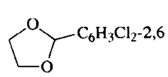
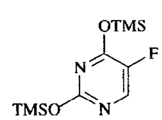
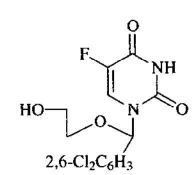
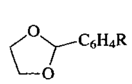
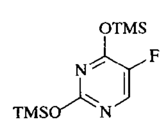
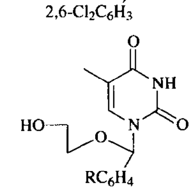
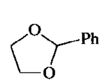
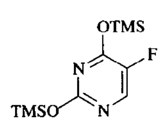
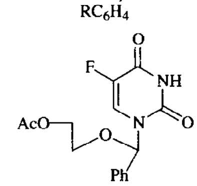
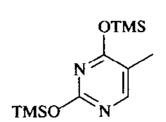
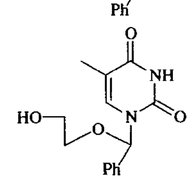
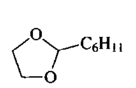
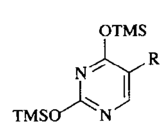
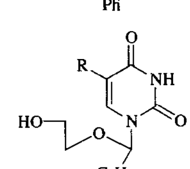
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, 30°, 4 h	 (25) + N^4-isomer (20)	666
		$SnCl_4$, CH_2Cl_2, 20°, 2 d	 (65)	661
		$SnCl_4$, MeCN, −20 to −25°, 24 h	 (84)	642
		$SnCl_4$, MeCN, rt, 1 h	 (—)	667
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 36 h 2. $NaHCO_3$ 3. NH_3, MeOH, 5°, 12 h	 (80)	660
C_9 		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (—)	637
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 R: *p*-Cl (30); *m*-NO_2 (14)	637
		1. $SnCl_4$, $CHCl_3$, rt, 1 h 2. $NaHCO_3$, MeOH 3. Ac_2O, rt, 3 h	 (27)	637
		$SnCl_4$, CH_2Cl_2, 20°, 2 d	 (63)	661
		$SnCl_4$, CH_2Cl_2	 R: F, rt, 12 h (37) Me, 20°, 2 d (73)	637 661

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

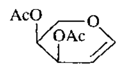
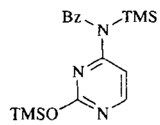
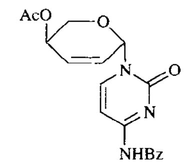
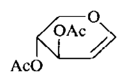
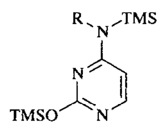
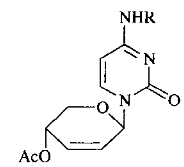
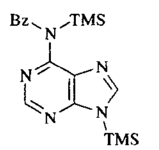
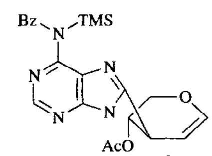
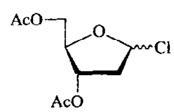
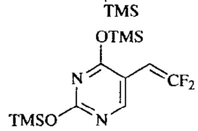
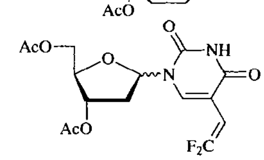
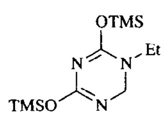
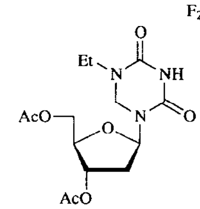
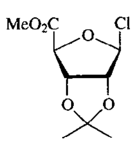
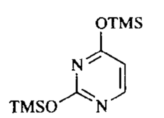
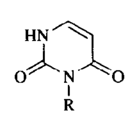
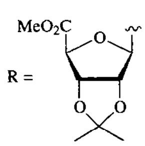
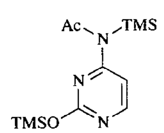
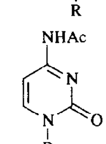
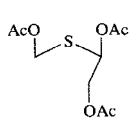
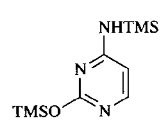
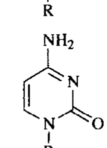
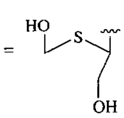
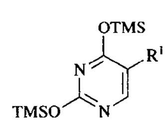
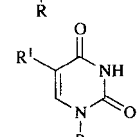
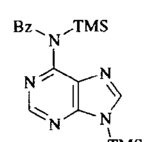
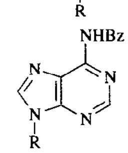
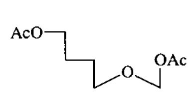
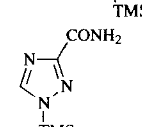
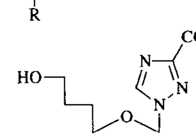
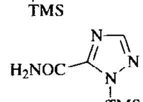
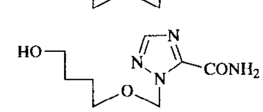
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$	 (—)	668
		$SnCl_4$, $Cl(CH_2)_2Cl$	 R: H (—); Bz (—)	668
		$SnCl_4$, $Cl(CH_2)_2Cl$	 (—) + α-anomer	668
		$SnCl_4$, $Cl(CH_2)_2Cl$, 4°, 16 h	 (—) α:β = 88:63	547
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, -25°, 5 min; 20°, 25 min	 (—)	669
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60°, 3 h	 (32) R = 	224
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60°, 4 h	 (33) + α-anomer (4) + N^3 isomer (7)	224
		1. $SnCl_4$ 2. NaOMe	 (63) R = 	670
		1. $SnCl_4$ 2. NaOMe	 R^1: F (49); I (63)	670
		$SnCl_4$	 (32)	670
		1. $SnCl_4$ 2. NH_3, MeOH	 (—)	653
		1. $SnCl_4$ 2. NH_3, MeOH	 (—)	653

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

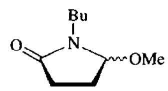
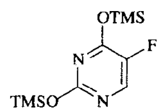
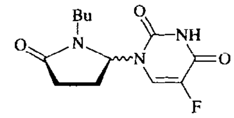
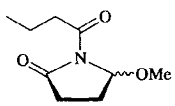
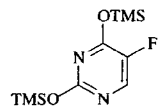
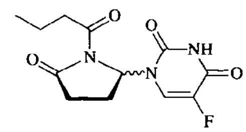
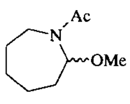
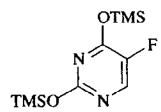
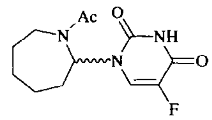
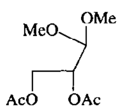
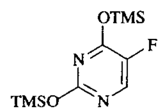
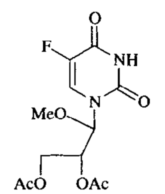
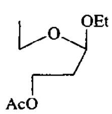
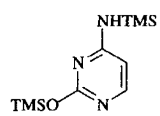
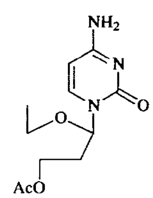
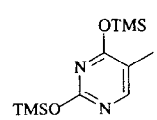
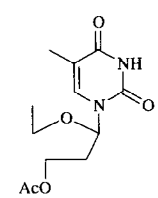
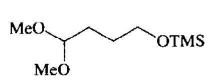
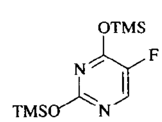
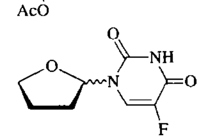
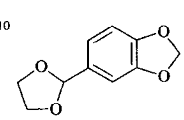
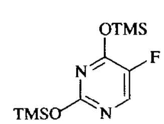
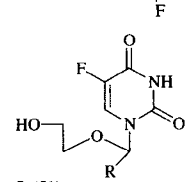
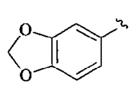
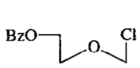
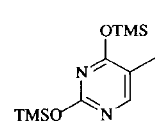
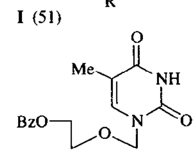
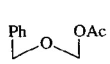
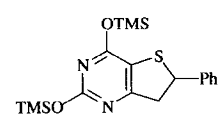
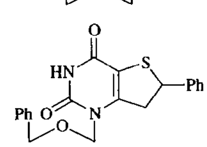
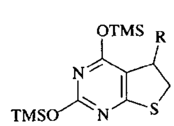
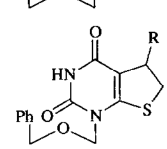
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, CH_2Cl_2, −20 to −25°, 6 h	 (38)	642
		$SnCl_4$, CH_2Cl_2, −13 to −15°, 3 h	 (78)	642
		$SnCl_4$, MeCN, −20 to −25°, 24 h	 (70)	642
		$SnCl_4$, MeCN, −78°, 15 min; 25°, 20 h	 (60)	663
		1. $SnCl_4$, MeCN, 30°, 1 d 2. NH_3, MeOH	 (88)	555
		1. $SnCl_4$, MeCN, 30°, 1 d 2. NH_3, MeOH	 (89)	555
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23–25°, 1 h	 (84)	671
C_{10} 		1. $SnCl_4$, CH_2Cl_2, rt, 12 h 2. $NaHCO_3$, MeOH	 I (29) R = 	637
		$SnCl_4$, CH_2Cl_2, rt, 3 h	I (51)	641
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 17 h	 (61)	643
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. NH_3, MeOH	 (20)	658
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. NH_3, MeOH	 R: H (41); Ph (33)	658

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

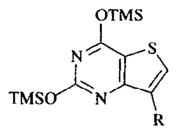
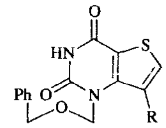
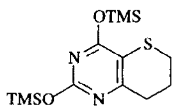
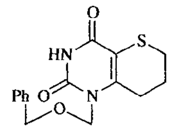
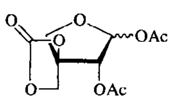
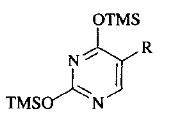
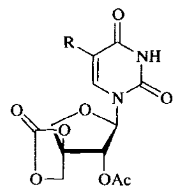
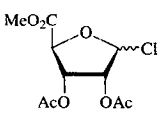
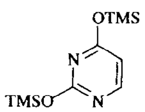
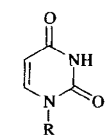
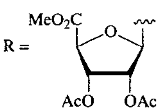
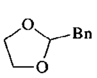
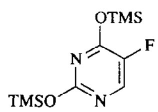
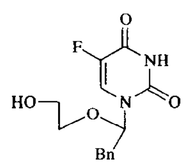
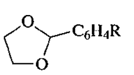
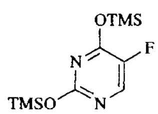
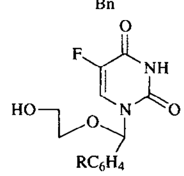
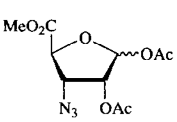
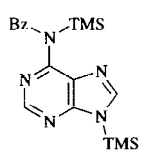
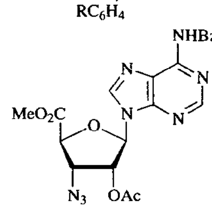
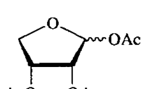
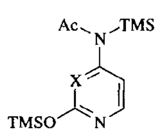
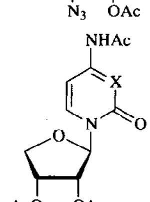
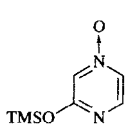
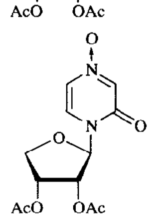
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, −30°, 8 h		659
	R			
	Me		(33)	
	Ph		(42)	
	p-FC_6H_4		(37)	
	p-ClC_6H_4		(34)	
	p-BrC_6H_4		(24)	
	p-MeC_6H_4		(32)	
	p-$MeOC_6H_4$		(32)	
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. NH_3, MeOH	 (46)	658
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 20 h	 R: Br (42); I (54)	672
		$SnCl_4$, $Cl(CH_2)_2Cl$, 25°, 20 h	 (39) + N^3-isomer R = 	224
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (45)	637
		$SnCl_4$, CH_2Cl_2, rt, time		637
			R / time: o-OMe 12 h (23); p-OMe 1 h (—); o-Me 12 h (30)	
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 4 h	 (57)	673
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, time		674
			X / time: CH 40 h (43); N 48 h (29)	
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 72 h	 (69)	674

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

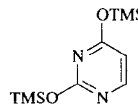
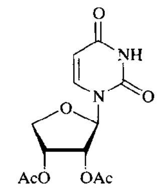
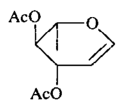
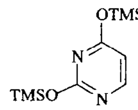
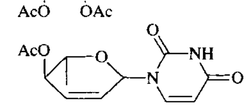
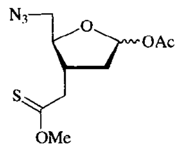
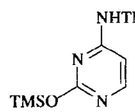
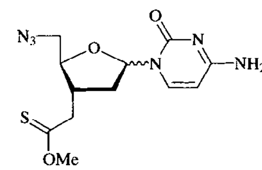
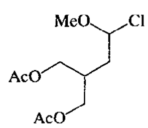
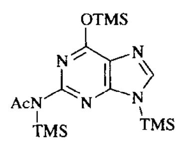
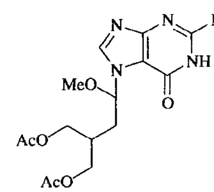
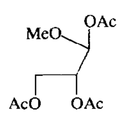
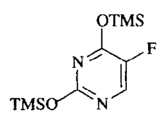
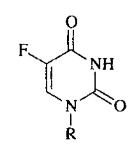
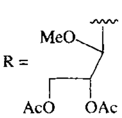
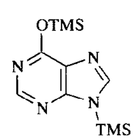
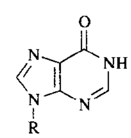
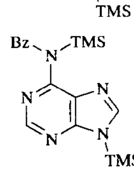
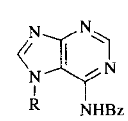
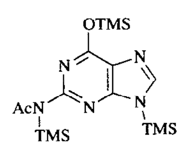
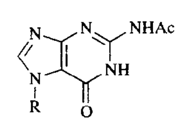
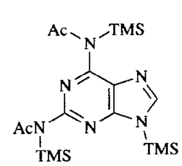
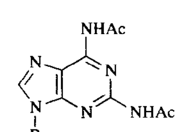
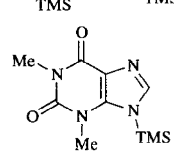
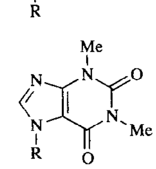
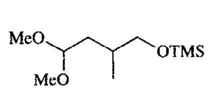
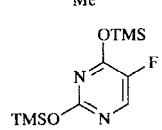
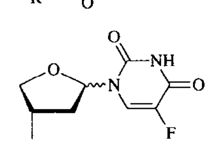
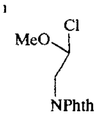
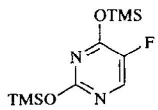
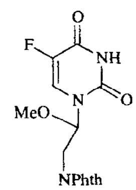
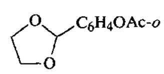
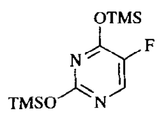
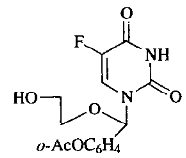
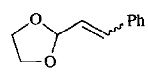
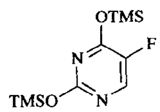
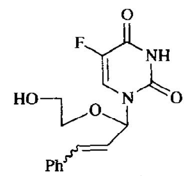
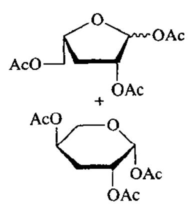
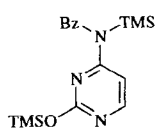
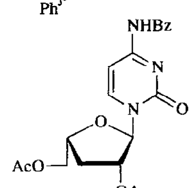
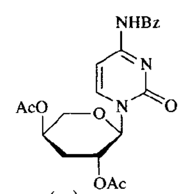
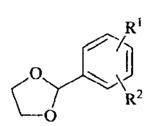
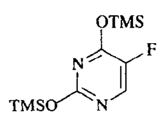
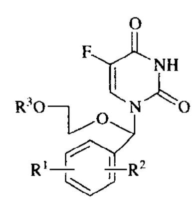
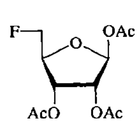
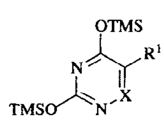
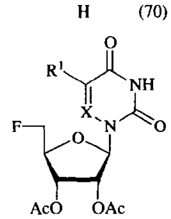
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (52)	674
		$SnCl_4$, $Cl(CH_2)_2Cl$, −15°, 2 h	 (60) α:β = 1.5:1	675
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt	 (—) α:β = 4:96	278
		$SnCl_4$, MeCN, 25°, 44 h	 (22) + N^9-isomer (16)	676
		$SnCl_4$, MeCN, −78°, 15 min; 25°, 18 h	 (57) R = 	663
		$SnCl_4$, MeCN, −78°, 15 min; 25°, 20 h	 (57) N^7, N^9 mixture	664
		$SnCl_4$, MeCN, −78°, 15 min; 25°, 20 h	 (40) + N^9-isomer (28)	664
		$SnCl_4$, MeCN, −78°, 15 min; 25°, 20 h	 (36) + N^9-isomer (9)	664
		$SnCl_4$, MeCN, −78°, 15 min; 25°, 20 h	 (31)	664
		$SnCl_4$, MeCN, −78°, 15 min; 25°, 20 h	 (27)	664
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23-25°, 1 h	 (72) α:β = 1:3	671

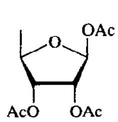
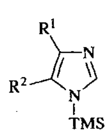
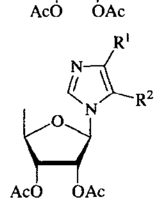
TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (32) + N^3-isomer (5)	677
		$SnCl_4$, CH_2Cl_2, rt, 1 h	 (47)	641
		$SnCl_4$, CH_2Cl_2, rt, 1 h	 (26)	637
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 5 h	 (—) +  (—)	678
		1. $SnCl_4$, CH_2Cl_2, rt, 12 h 2. (see below) 3. (see below)		637

R^1	R^2	2	3	R^3	
o-OEt	H	—	—	H	(20)
o-OAc	H	$NaHCO_3$,	Ac_2O, Py	Ac	(—)
p-OEt	H	—	—	H	(18)
o-OMe	*m*-OMe	—	—	H	(13)
p-OMe	*m*-OMe	—	—	H	(43)
p-OAc	*m*-OMe	—	—	H	(70)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 4.5 h		679

R^1	X	
Me	CH	(70)
H	N	(31)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, time		680

R^1	R^2	time	
CO_2Me	CH_2CN	9 h	(68)
CH_2CN	CO_2Me	48 h	(48) + N^3-isomer (26)

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

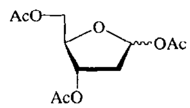
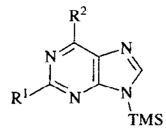
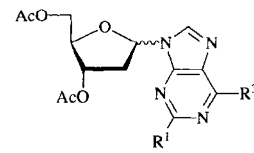
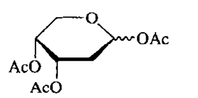
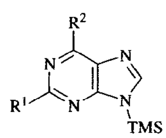
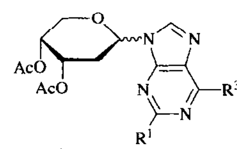
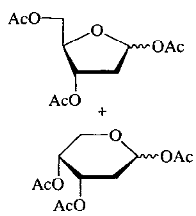
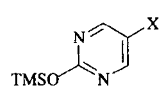
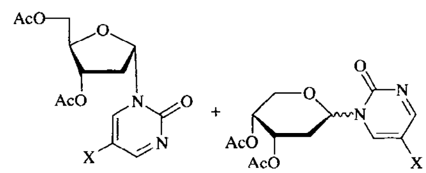
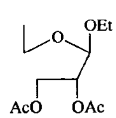
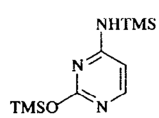
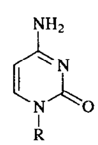
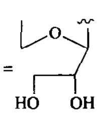
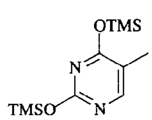
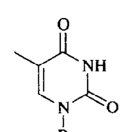
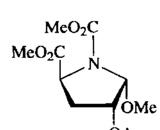
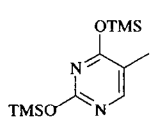
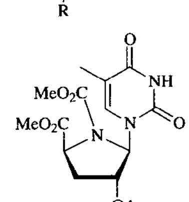
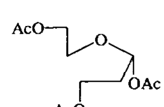
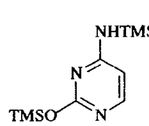
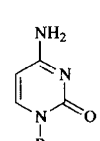
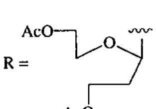
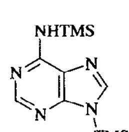
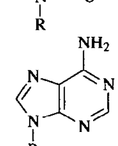
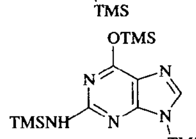
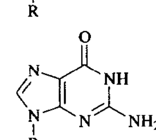
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
				515
	R^1 / R^2		R^3 / α:β	
	H / BzNTMS	$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	NHBz (60) 68:32	
	H / BzNTMS	$SnCl_4$, MeCN, rt, 12 h	NHBz (95) 78:22	
	AcNTMS / O_2CNPh_2	$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 16 h	O_2CNPh_2 (40) 75:25	
	AcNTMS / O_2CNPh_2	$SnCl_4$, MeCN, rt, 16 h	O_2CNPh_2 (80) 68:32	
		$SnCl_4$, MeCN, rt, 12 h		515
	R^1 / R^2		R^3 / α:β	
	H / BzNTMS		NHBz (85) 52:48	
	AcNTMS / O_2CNPh_2		O_2CNPh_2 (80) 60:40	
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 5-12 h		681
			X: Br (2) + (1)	
			X: I (11) + (15)	
		1. $SnCl_4$, MeCN, 30°, 1 d 2. NH_3, MeOH	 (80) R = 	555
		1. $SnCl_4$, MeCN, 30°, 1 d 2. NH_3, MeOH	 (82)	555
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0°, 3 h	 (19) + α-anomer (7)	45c
		$SnCl_4$, MeCN, 25-30°, 24 h	 (73) R = 	682
		$SnCl_4$, MeCN, 25-30°, 24 h	 (80)	682
		$SnCl_4$, MeCN, 25-30°, 24 h	 (76)	682

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

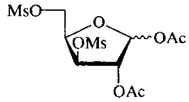
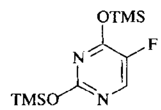
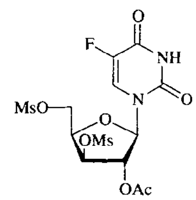
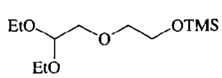
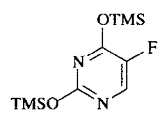
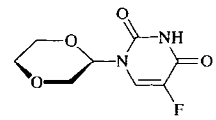
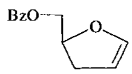
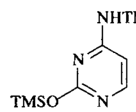
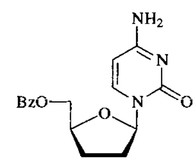
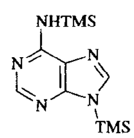
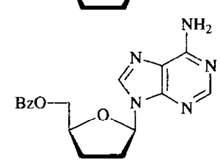
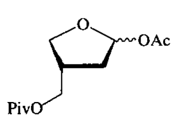
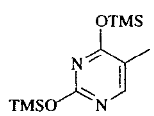
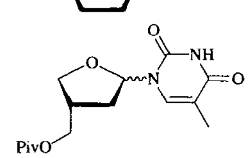
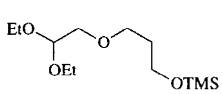
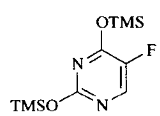
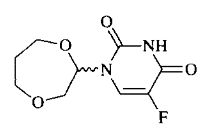
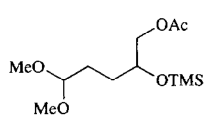
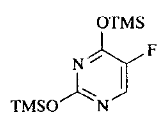
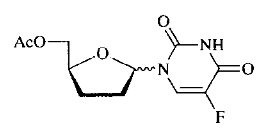
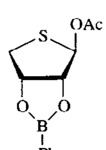
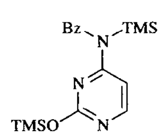
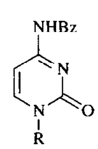
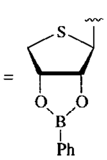
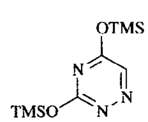
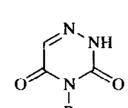
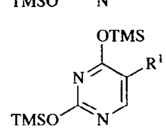
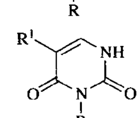
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, rt, 4 h	 (59)	683
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23-25°, 1 h	 (75)	671
C_{12} 		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 5 h	 (—)	684
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 5 h	 (—)	685
		$SnCl_4$, $Cl(CH_2)_2Cl$, –50°, 2 h	 (40) α:β = 1:3	139a
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23 to 25°, 1 h	 (28)	671
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23 to 25°, 1 h	 (67) α:β = 5:1	671
		$SnCl_4$	 (57) R = 	686, 687
		$SnCl_4$	 (42)	686, 687
		$SnCl_4$, CH_2Cl_2, rt, 12 h		687
	R^1			
	H		(65)	
	F		(40)	
	Br		(60)	
	I		(57)	
	Me		(55)	

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

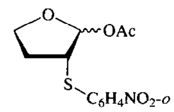
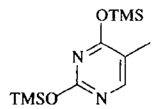
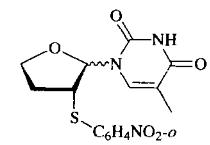
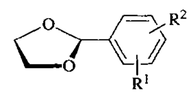
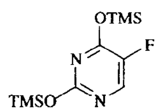
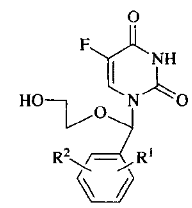
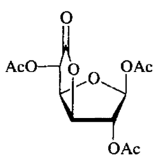
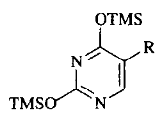
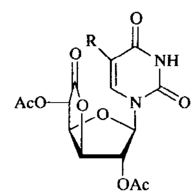
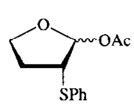
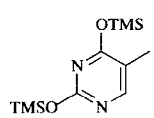
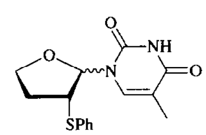
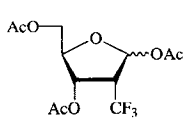
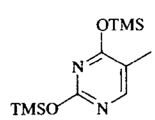
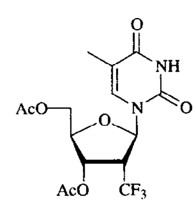
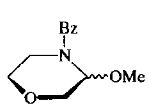
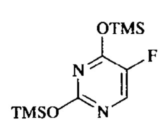
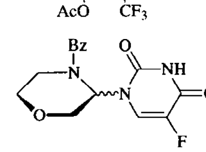
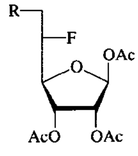
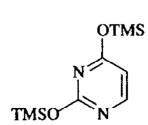
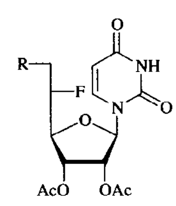
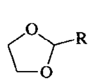
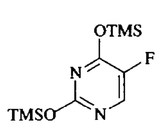
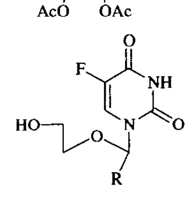
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, CH_2Cl_2, –78 to 25°, 5 h	 (—) α:β = 1:16	227
		$SnCl_4$, CH_2Cl_2, rt, 12 h		637
R^1 / R^2				
o-$OCH_2CH{=}CH_2$ / H			(49)	
p-$OCH_2CH{=}CH_2$ / H			(47)	
o-CO_2Et / H			(42)	
p-OAc / m-OMe			(70)	
				
	R			
	F	$SnCl_4$, CH_2Cl_2, rt, 12 h	(35)	688
	F	$SnCl_4$	(75)	688
	Br	$SnCl_4$	(60)	688
	I	$SnCl_4$	(56)	688
		$SnCl_4$, CH_2Cl_2, –78 to 25°, 5 h	 I (—) α:β = 1:17	227
		$SnCl_4$, CH_2Cl_2, 25°	I (—) α:β = 1:30	227
		$SnCl_4$, MeCN, 50°	 (40) α:β = 1:12	689
		$SnCl_4$, MeCN, –20 to –25°, 24 h	 (71)	642
		$SnCl_4$	 R: F (—); N_3 (—)	690
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 R: C_6H_4(Pr-*i*)-*p* (24); $C_6H_2(OMe)_3$-3,4,5 (—)	637

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

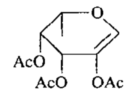
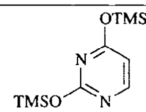
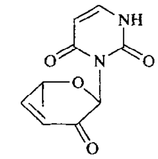
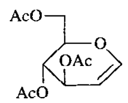
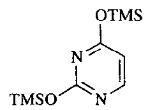
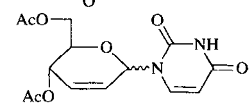
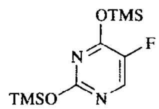
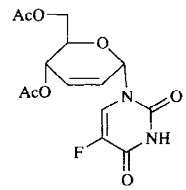
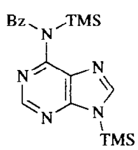
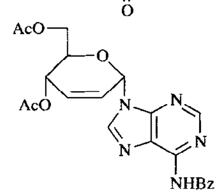
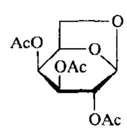
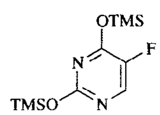
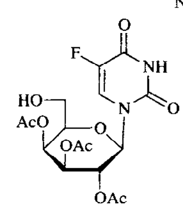
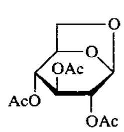
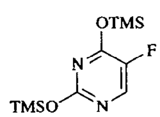
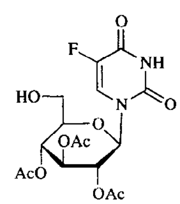
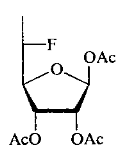
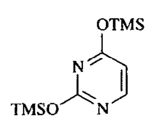
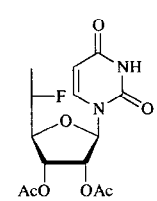
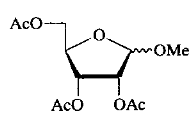
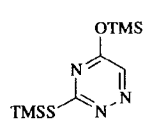
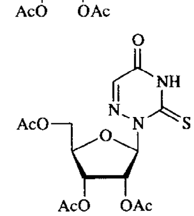
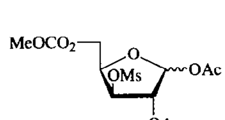
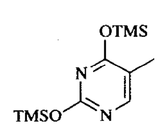
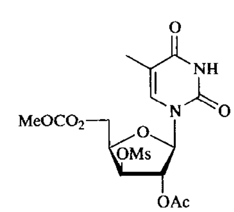
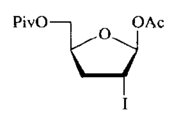
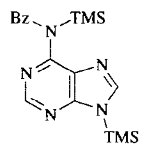
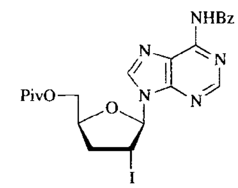
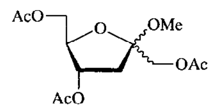
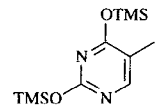
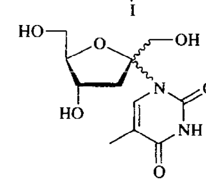
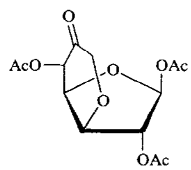
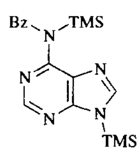
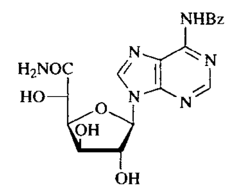
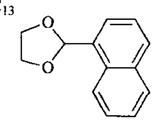
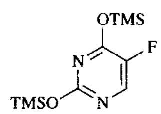
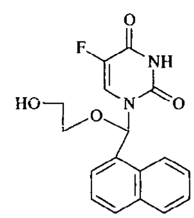
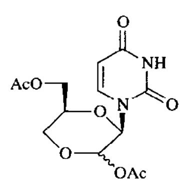
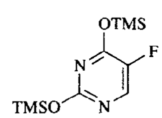
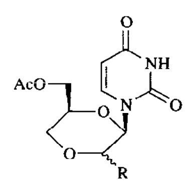
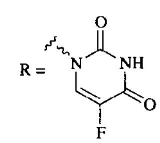
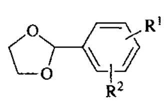
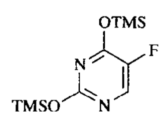
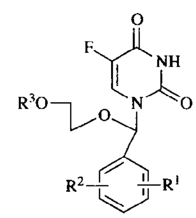
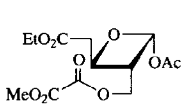
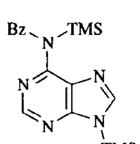
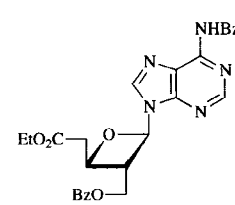
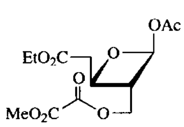
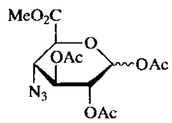
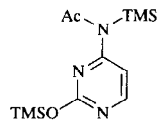
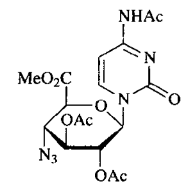
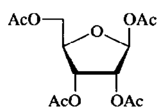
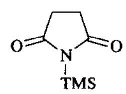
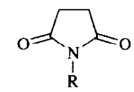
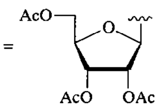
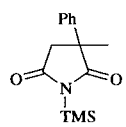
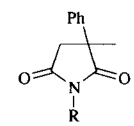
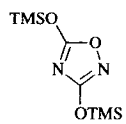
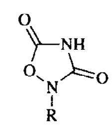
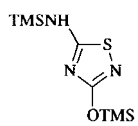
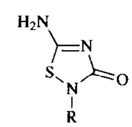
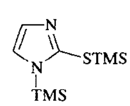
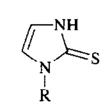
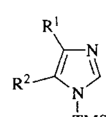
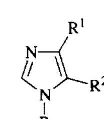
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, CH_2Cl_2, 0°, 6 h	 (50)	675
		$SnCl_4$, MeCN	 (78)	105
		$SnCl_4$, MeCN, rt, 35 min	 (36) + β-anomer (22)	306
		$SnCl_4$, MeCN, rt, 2 h	 (18)	306
		$SnCl_4$, MeCN, reflux, 10 h	 (60)	692
		$SnCl_4$, MeCN, reflux, 10 h	 (80)	692
		$SnCl_4$	 (—)	690
		$SnCl_4$, $Cl(CH_2)_2Cl$, 22°, 5 h	 (73)	84
		$SnCl_4$, CH_2Cl_2, rt, 18 h	 (66)	545

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, −20° to rt	 (45)	423
		1. $SnCl_4$, MeCN, −20° to rt, 1 h 2. NH_3, MeOH	 (41) α:β = 1:2	693
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 48-72 h 2. NH_3, MeOH	 (64)	101
C_{13} 		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (44)	637
		$SnCl_4$, MeCN, rt	 (30) R = 	694
		1. $SnCl_4$, CH_2Cl_2, rt, 12 h 2. (see below) 3. (see below)		637
		1. $SnCl_4$, $Cl(CH_2)_2Cl$ 2. NaOMe 3. BzCl, Py	 I (26) + α-anomer (9)	233
	"	1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 30 min 2. NaOMe, MeOH 3. BzCl, Py, CH_2Cl_2, rt, 12 h	I (16) + α-anomer (10)	233

R^1	R^2	2	3	R^3	Yield
p-OAc	*m*-OAc	$NaHCO_3$, MeOH	Ac_2O, Py, rt, 3 h	Ac	(—)
o-OAc	*m*-OAc	—	—	H	(53)
p-$OCH_2CH=CH_2$	*m*-OMe	—	—	H	(51)
p-OAc	*m*-OEt	—	—	H	(41)
p-OPr-*n*	H	—	—	H	(19)

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60°, 12 h	 (67)	695, 696
		$SnCl_4$, MeCN, rt, 24 h	 (86) R = 	548, 697
		$SnCl_4$, MeCN, 35-40°, 18 h	 (48)	698
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 16 d	 (70)	699
		$SnCl_4$, $Cl(CH_2)_2Cl$, 25°, 5 h	 (60)	700
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 8 d	 **I** (34) + bis(product) **II** (64)	701
		$SnCl_4$, MeCN, rt, 8 d	**I** (28) + bis(product) **II** (66)	701
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 45 min	**I** (42) + bis(product) **II** (52)	701
		$SnCl_4$, $Cl(CH_2)_2Cl$		

R^1	R^2	Conditions	R^1	R^2		N^3-isomer	Refs.
NO_2	Br	rt, 18 h	NO_2	Br	(33)	(14)	702
Me	CN	rt, 24 h	Me	CN	(38)	(16)	703
CO_2Me	CH_2CN	rt, 16-20 h	CO_2Me	CH_2CN	(95)	(—)	704
		rt, 6 h	CO_2Me	CH_2CN	(38)	(19) - β-isomer	705
		—	CH_2CN	CO_2Me	(35)	(30)	706
		rt, 6 h	CH_2CN	CO_2Me	(57)	(—)	707
CO_2Et	Me	reflux, 2 h	CO_2Et	Me	(43)	(6)	708
		reflux	CO_2Et	Me	(43)	(—)	709
TMSO	$CONH_2$	CH_2Cl_2, rt, 12 h	$CONH_2$	OH	(—)	(—)	710

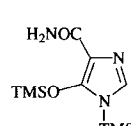
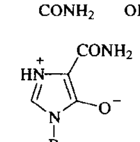
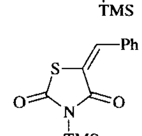
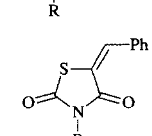
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$	 (14)	241
		$SnCl_4$, MeCN	 (—)	711

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

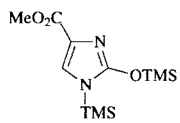
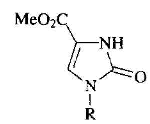
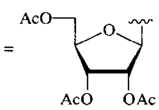
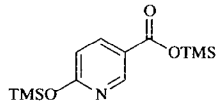
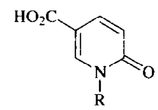
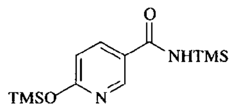
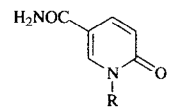
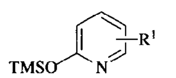
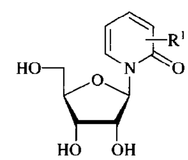
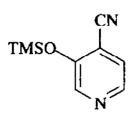
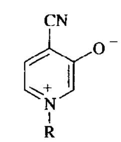
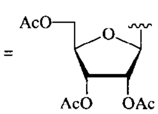
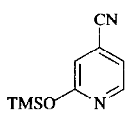
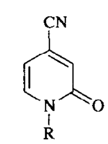
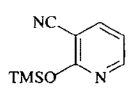
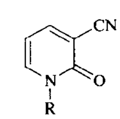
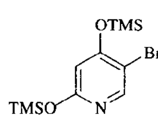
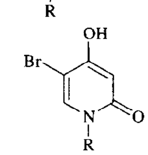
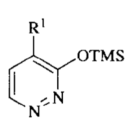
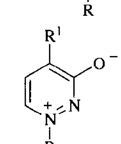
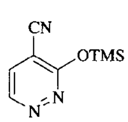
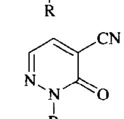
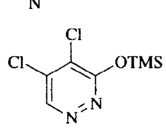
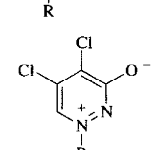
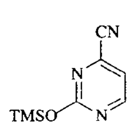
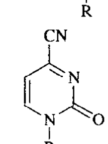
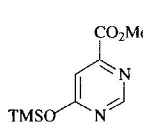
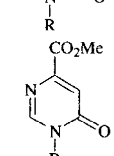
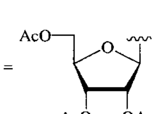
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$	 (36) R = 	712
		$SnCl_4$, MeCN, rt, 20 h	 (88)	713
		$SnCl_4$, MeCN, $Cl(CH_2)_2Cl$, rt, 16 h	 (85)	713
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 8 h; rt, 12 h 2. NH_3, MeOH, 0°, 4 d	 R^1: 3-NO_2 (51); 5-NO_2 (80)	714
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0-5°, 1 h	 (57) R = 	715
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0-5°, 30 min; rt, 15 h	 (86)	715
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 8 h; rt, 12 ht 2. NH_3, MeOH, 0°, 4 d	 (48)	714
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h	 (97)	716
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 30 min	 R^1: Cl (77); CN (85); CO_2Et (45)	253
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 15 min	 (51)	253
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 30 min	 (76)	253
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 2 h	 (73)	715
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 45 min	 (80-90) R = 	715

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

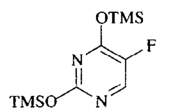
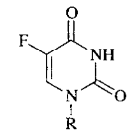
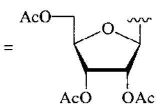
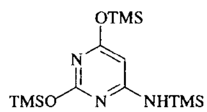
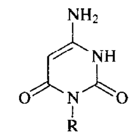
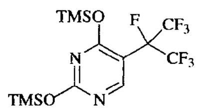
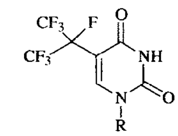
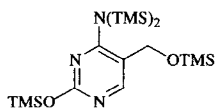
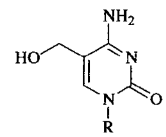
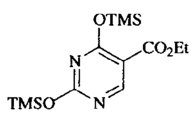
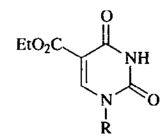
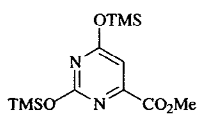
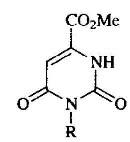
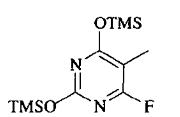
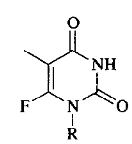
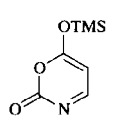
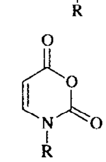
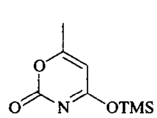
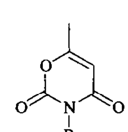
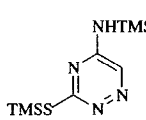
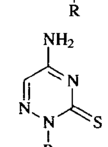
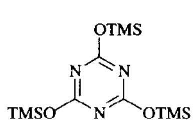
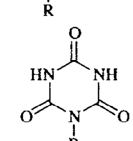
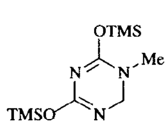
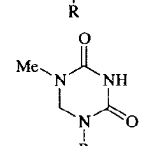
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, rt, 3 h	 (81) R = 	514b
		$SnCl_4$	 (—)	717
		$SnCl_4$	 (—)	718
		$SnCl_4$, MeCN	 (—)	719
		$SnCl_4$, CH_2Cl_2, rt, 30 min	 (55)	542
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 72 h	 (40) + N^1,N^3-bis(isomer) (14)	720
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 8 h	 (—)	721
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 2.5 h	 (91)	722
		$SnCl_4$	 (94)	723
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 16 h	 (59)	724
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23°, 4 h	 (77)	725
		$SnCl_4$, $Cl(CH_2)_2Cl$, 25°, 72 h	 (4)	239

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

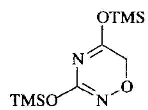
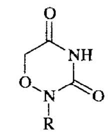
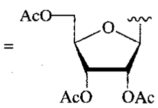
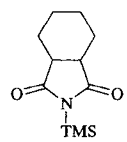
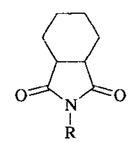
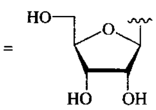
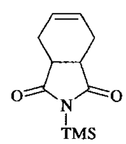
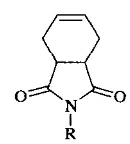
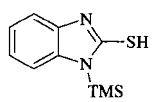
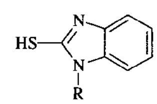
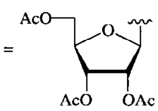
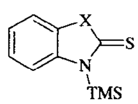
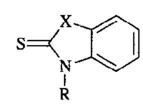
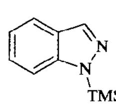
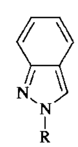
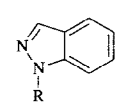
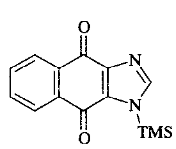
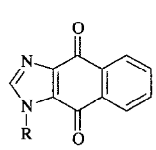
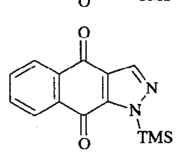
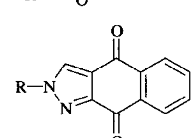
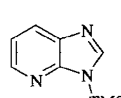
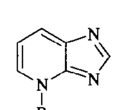
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 (86) R = 	726
		1. $SnCl_4$ 2. HCl, MeOH	 (16) R = 	697
		1. $SnCl_4$ 2. HCl, MeOH	 (37)	697
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 7 d	 (34) + bis(riboside) (12) R = 	727
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 7 d	 X: O (30); S (34)	727
		$SnCl_4$ (0.2 eq), MeCN, rt	 I (62) + N^1-isomer (4)	728
		$SnCl_4$ (0.2 eq), MeCN, reflux	I (44) + N^1-isomer (9)	728
		$SnCl_4$ (1 eq), MeCN, rt	 I (10)	728
		$SnCl_4$ (1 eq), MeCN, reflux	I (7)	728
		$SnCl_4$ (0.5 eq), MeCN, reflux	I (41)	728
		$SnCl_4$ (0.5 eq), MeCN, rt	I (39)	728
		$SnCl_4$ (1.5 eq), MeCN, rt	I (6)	728
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 3 h	 (54)	729
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 3 h	 (76)	729
		$SnCl_4$ (2.5 eq), MeCN, rt, 5 h	 I (60) + N^3-isomer (24)	625
		$SnCl_4$ (1.1 eq), MeCN, rt, 5 h	I (70) + N^3-isomer (17)	625

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

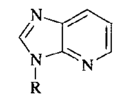
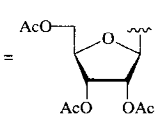
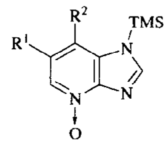
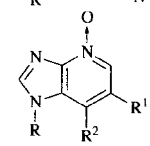
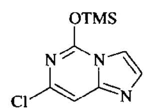
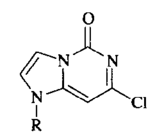
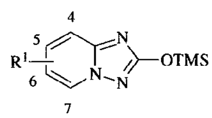
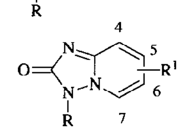
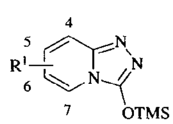
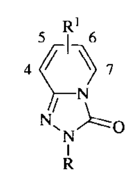
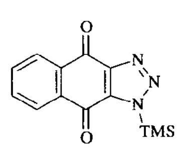
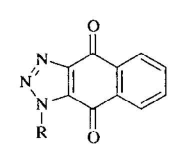
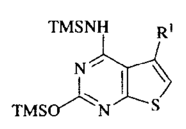
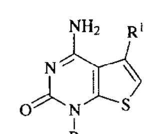
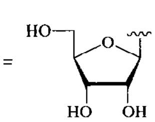
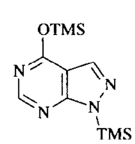
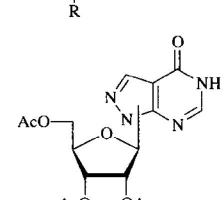
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$ (1.1 eq), MeCN, rt, 30 h	**I** (62) + N^3-isomer (16) + N^1-isomer (11)	625
		$SnCl_4$ (3.6 eq), MeCN, rt, 30 h	 (42) + N^4-isomer (15) + N^1-isomer (26) R = 	625
		$SnCl_4$, MeCN, rt		
	R^1 R^2			
	H H	6 h	(83)	730-732
	H Cl	6 h	(82)	730,731
	Br H	18 h	(79)	732
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 (64)	733
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux		734
	R^1			
	4-Me	10 h	(47)	
	5-Me	8 h	(25)	
	6-Me	8 h	(50)	
	7-Me	10 h	(73)	
	5,7-Me_2	8 h	(57)	
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux		734
	R^1			
	H	2 h	(96)	
	4-Me	10 h	(48)	
	5-Me	8 h	(37)	
	6-Me	8 h	(21)	
	5,7-Me_2	8 h	(2)	
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 3 h	 (44)	729
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 4 h 2. NH_3, MeOH, rt, 20 h	 R^1: H (48); Me (60) R = 	525
		$SnCl_4$, $Cl(CH_2)_2Cl$, MS, 60°, 4.5 h	 **I** (25) mixture of N^1-, N^2-, and N^5-isomers + N^1,N^5-bis(riboside) (23) + N^2,N^5-bis (riboside) (12)	510
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60°, 4 h	**I** 3 monoriboside isomers + N^2,N^5- and N^1,N^5-bis(ribosides), 2:2:1	735

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

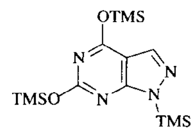
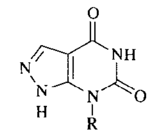
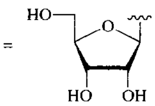
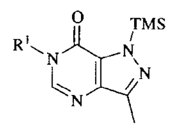
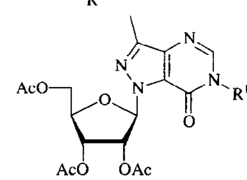
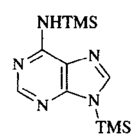
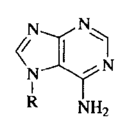
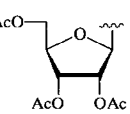
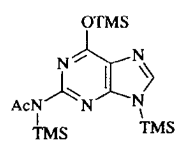
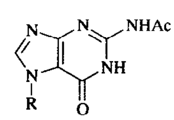
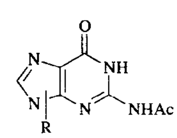
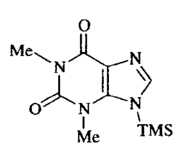
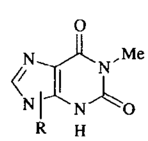
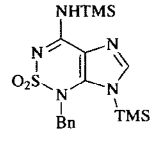
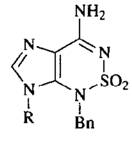
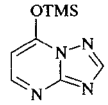
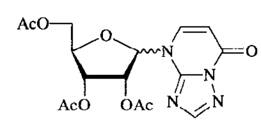
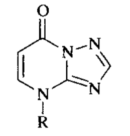
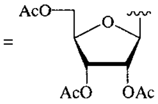
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 1 h 2. NH_3, MeOH	 (—) R = 	736
		$SnCl_4$, MeCN, 25°, 18 h		737
	R^1			
	Bu		(75)	
	i-C_5H_{11}		(80)	
	Bn		(72)	
	p-ClC_6H_4		(65)	
	p-$ClC_6H_4CH_2$		(70)	
	p-MeC_6H_4		(66)	
	$BnCH_2$		(73)	
	p-$MeOC_6H_4CH_2$		(75)	
		$SnCl_4$, MeCN, rt, 20 h	 (25) + α-anomer (18) + N^9-isomer (20) R = 	625
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (70)	141
		$SnCl_4$, MeCN, rt, 20 h	 (78) N^7:N^9 = 95:1	142
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 30 min	 (—) N^7:N^9 = 4:1	738
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (15)	739
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 2 h	 (49) α:β = 1:2.4 + N^3-isomer (21), α:β = 1:1.5	257
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 4 h	 (46) + N^3-isomer (10) R = 	257

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

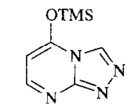
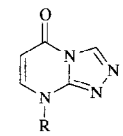
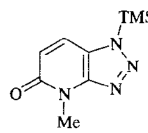
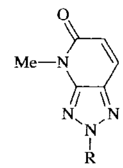
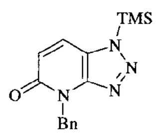
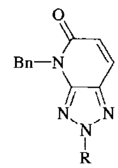
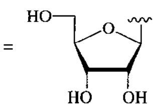
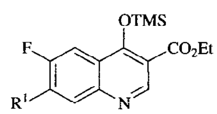
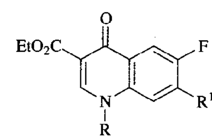
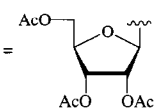
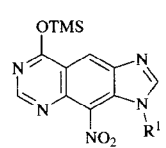
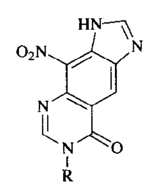
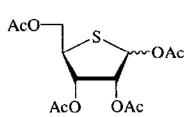
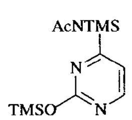
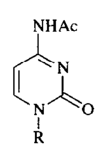
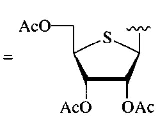
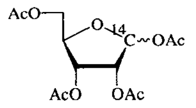
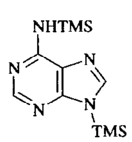
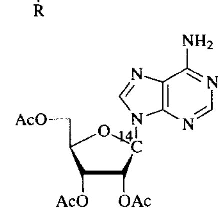
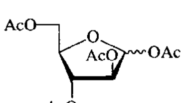
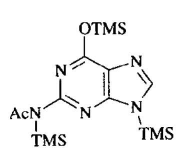
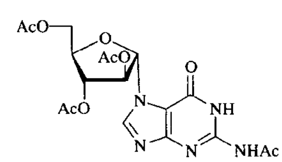
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 4 h	 (52) + N^1-isomer (11)	257
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 6 h; rt, 18 h	 (—)	714
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 8 h; 21°, 16 h 2. NaOMe, MeOH, rt, 16 h	 (78) R = 	714
	 R^1 H F Cl	$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 3 h	 R =  (19) (25) (15)	740
	 R^1 H TMS	$SnCl_4$ CH_2Cl_2, rt, 30 min MeCN, rt, 15 h	 (22-35) (19) + N^1-isomer (9) + N^3-isomer (7)	509
		$SnCl_4$, $Cl(CH_2)_2Cl$, 25°, 20 h	 (65) + α-anomer (3) R = 	215
		$SnCl_4$, MeCN	 (80)	741
		$SnCl_4$, $Cl(CH_2)_2Cl$, 80°, 12 h	 (82)	141a

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

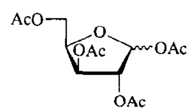
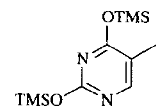
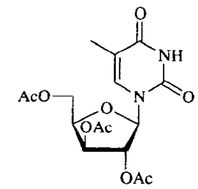
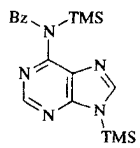
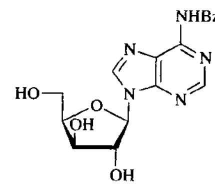
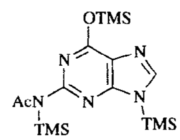
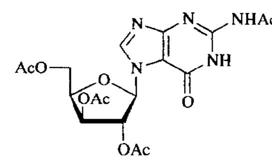
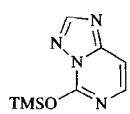
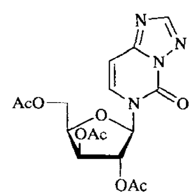
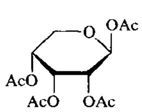
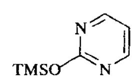
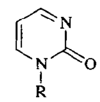
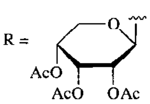
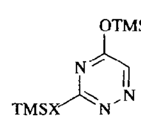
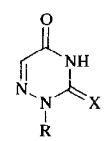
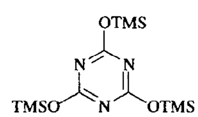
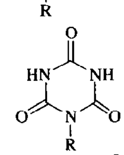
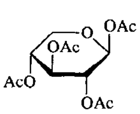
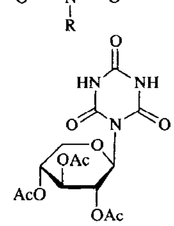
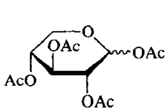
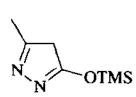
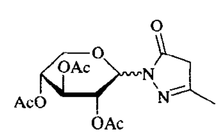
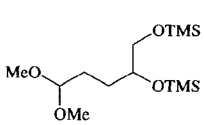
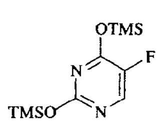
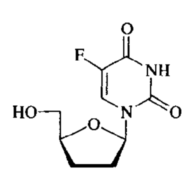
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, CH_2Cl_2, rt, 18 h	 (83)	742
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 48-72 h 2. NH_3, MeOH	 (50-70) + N^7-isomer	101
		$SnCl_4$, $Cl(CH_2)_2Cl$, 24°, 24 h	 (76) + N^9-isomer (3)	141a
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 (65)	743
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 1 h	 (69) R = 	744
		$SnCl_4$, $Cl(CH_2)_2Cl$	 X: O, C_6H_6, 22°, 8 h (73); S, 50°, 3 h (82)	84
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23°, 55 h	 (59)	745
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23°, 6 h	 (63) + N^1,N^3-bis(isomer) (19)	745
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 (26)	746
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23-25°, 1 h	 (62)	677

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

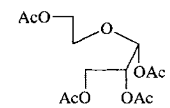
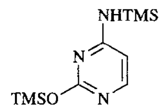
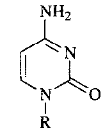
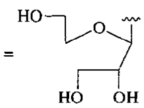
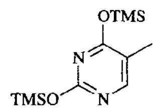
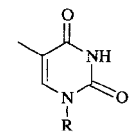
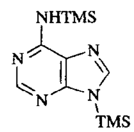
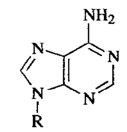
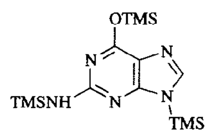
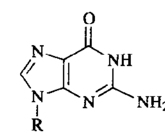
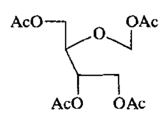
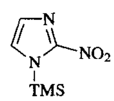
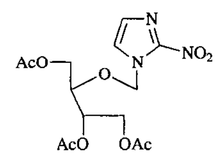
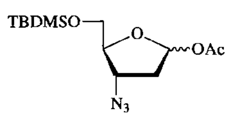
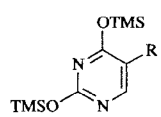
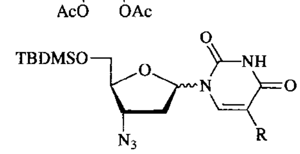
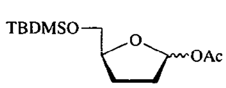
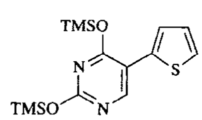
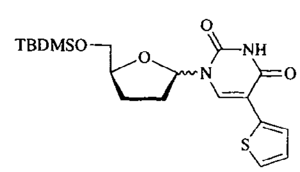
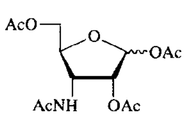
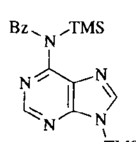
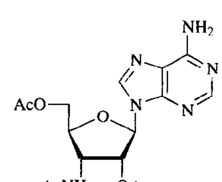
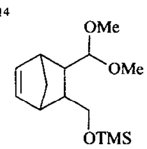
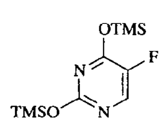
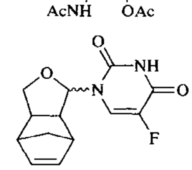
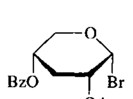
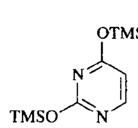
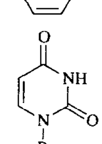
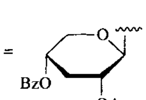
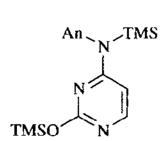
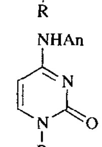
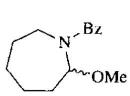
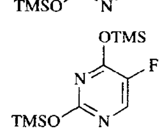
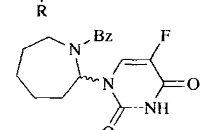
Sugar	Base	Conditions	Product(s) and Yield(s) (%)		Refs.
		1. $SnCl_4$, MeCN, 30°, 48 h 2. NH_3, MeOH	 (66)	R = 	747
		1. $SnCl_4$, MeCN, 30°, 48 h 2. NH_3, MeOH	 (67)		747
		1. $SnCl_4$, MeCN, 30°, 48 h 2. NH_3, MeOH	 (71)		747
		1. $SnCl_4$, MeCN, 30°, 48 h 2. NH_3, MeOH	 (84)		747
		$SnCl_4$, MeCN, 2-3 h	 (81)		748
		$SnCl_4$, MeCN, rt, 18 h		R H (82) α:β = 66:34 Me (68) α:β = 1:1	749
		1. $SnCl_4$, MeCN, –15° 2. NH_3, MeOH, rt		(—) α:β = 1:2.1	750
		$SnCl_4$, $Cl(CH_2)_2Cl$, 80°, 18 h	 (55)		751
C_{14} 		$SnCl_4$, $Cl(CH_2)_2Cl$, 23-25°, 1 h	 (61)		671
		$SnCl_4$, MeCN, rt, 3 h	 (50)	R = 	752
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 1 h; 60°, 20 min	 (43)		752
		$SnCl_4$, MeCN, –20 to –25°, 24 h	 (73)		642

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

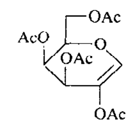
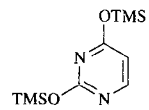
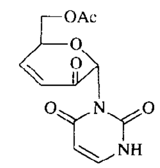
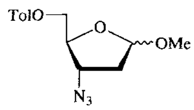
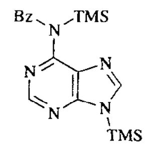
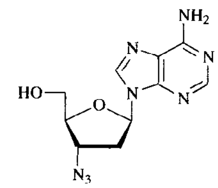
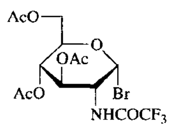
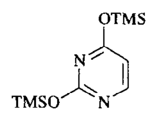
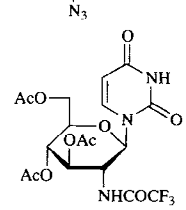
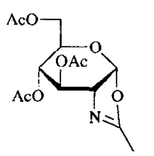
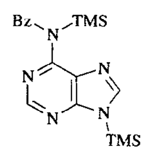
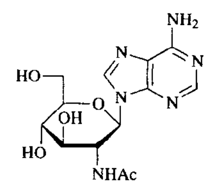
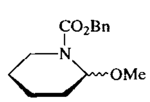
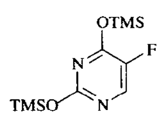
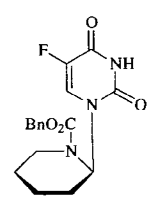
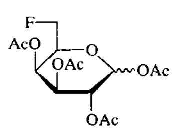
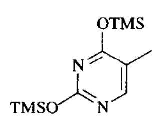
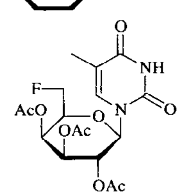
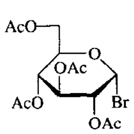
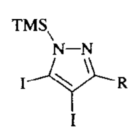
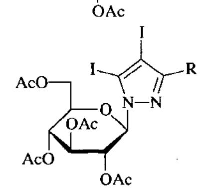
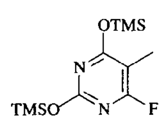
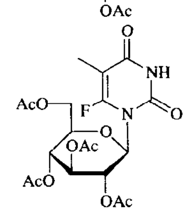
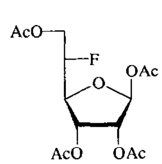
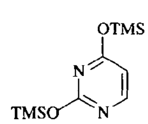
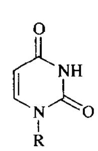
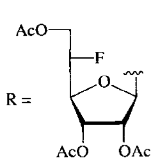
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, CH_2Cl_2, 0°, 6 h	 (65)	675
		1. $SnCl_4$, MeCN, reflux, 3 h 2. NH_3, MeOH, rt, 24 h	 (34)	279
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 4 h	 (80)	218
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 50-60°, 5 h 2. *n*-$BuNH_2$, MeOH	 (58)	100
		1. $SnCl_4$, MeCN, –40 to –45°, 10 min 2. $NaHCO_3$	 (54)	642
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 3 h	 (29)	753
		$SnCl_4$, $Cl(CH_2)_2Cl$, 40°, 2 h	 R: I (75); Me (72)	754
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 5 h	 (75)	540
		$SnCl_4$	 (—) R = 	690

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

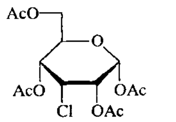
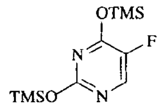
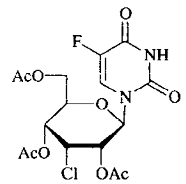
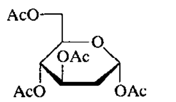
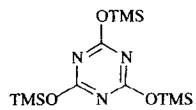
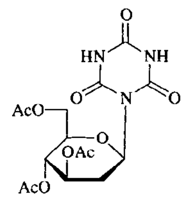
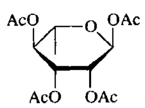
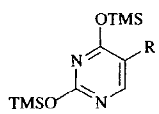
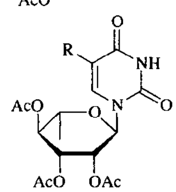
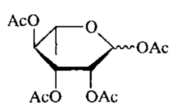
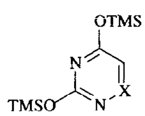
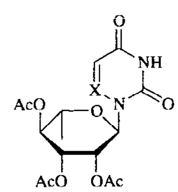
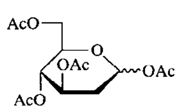
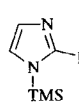
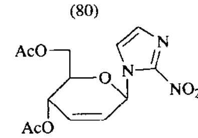
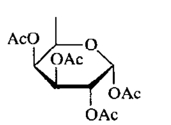
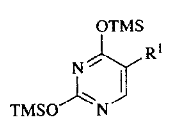
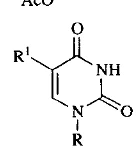
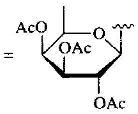
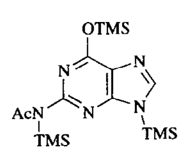
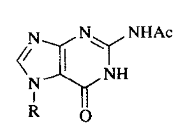
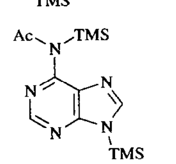
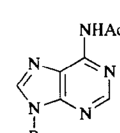
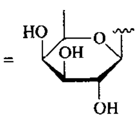
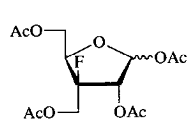
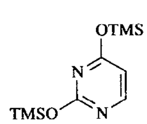
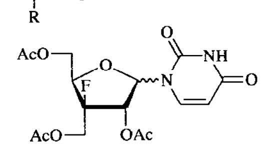
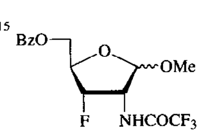
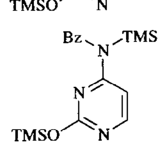
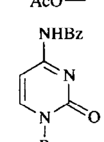
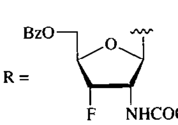
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (75)	755
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23°, 15 min	 (55) + N^1,N^3-bis(product) (12)	745
		$SnCl_4$, $Cl(CH_2)_2Cl$		
	R			
	F	rt, 5 h	(85)	756
	Cl	60°	(67)	757
		$SnCl_4$, $Cl(CH_2)_2Cl$		
	X			
	CH	rt, 3 h	(—)	758
	N	50°, 2.5 h	(80)	759
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 45 min	 (15) + α-anomer (5)	760
		$SnCl_4$, MeCN, rt, 6 h	 R^1: H (95); Me (98) R = 	761
		$SnCl_4$, MeCN, reflux, 6 h	 (52)	761
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 2 h 2. NH_3, MeOH	 (94) R = 	761
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 24 h	 (—) α:β = 1:1.8	762
C_{15} 		$SnCl_4$, MeCN, reflux, 2 h	 (82) R = 	763

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

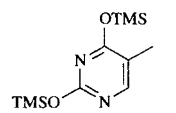
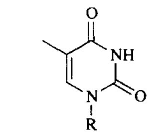
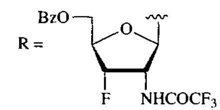
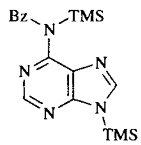
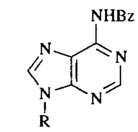
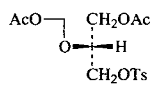
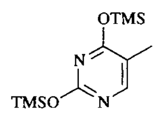
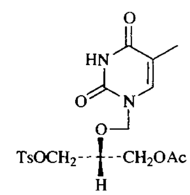
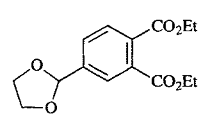
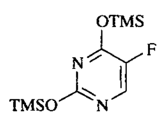
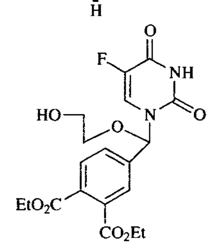
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, reflux, 45 min	 (63) R = 	763
		$SnCl_4$, MeCN, reflux, 30 min	 (53)	763
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt	 (42)	764
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (46)	637

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

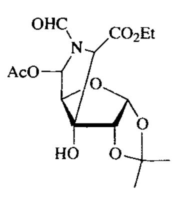
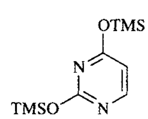
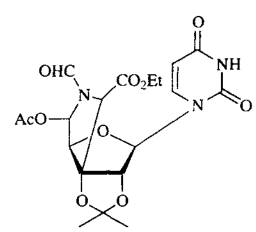
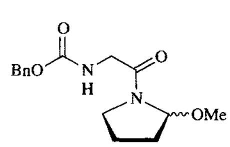
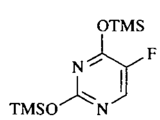
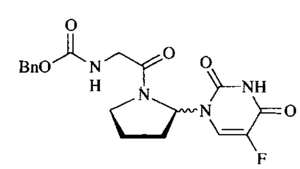
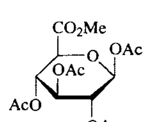
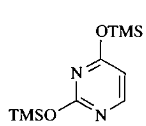
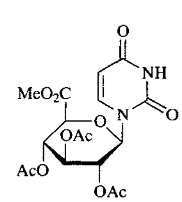
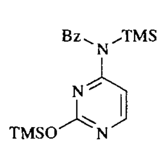
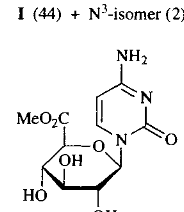
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 (72)	765
		$SnCl_4$, CH_2Cl_2, −13 to −15°, 3 h	 (72)	642
		$SnCl_4$, $Cl(CH_2)_2Cl$, 70°, 5 h	 I (15) + N^3-isomer (10)	766
		$SnCl_4$, MeCN, rt, 24 h	I (44) + N^3-isomer (2)	767
		1. $SnCl_4$ (1.3 eq) 2. NH_3, MeOH	 (70)	768

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

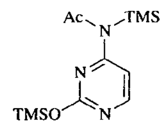
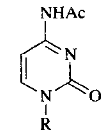
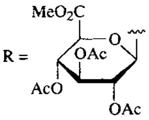
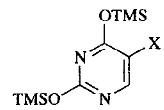
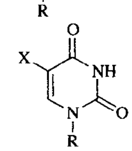
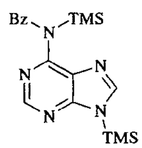
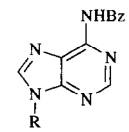
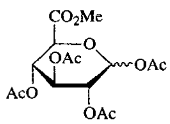
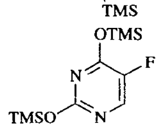
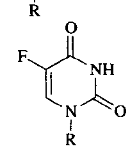
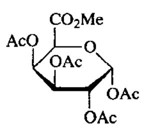
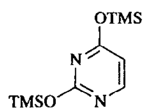
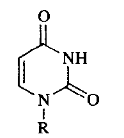
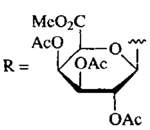
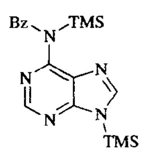
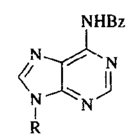
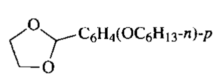
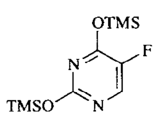
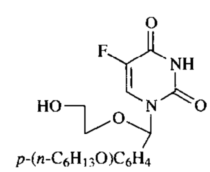
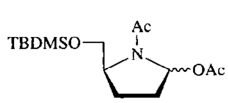
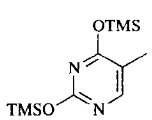
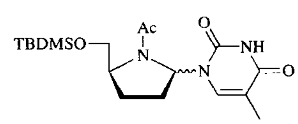
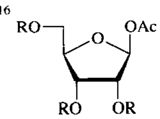
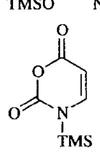
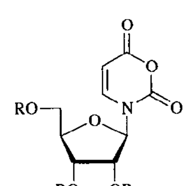
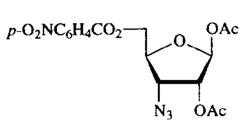
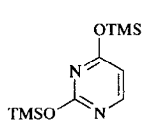
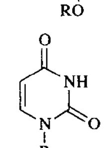
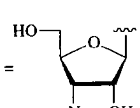
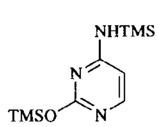
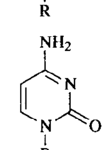
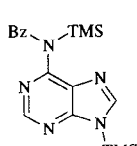
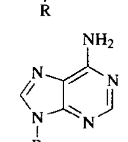
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h 2. reflux, 1 h	 (17) R = 	769
		$SnCl_4$, MeCN, rt, 24 h	 X: F (80); Cl (63); Br (61); I (55)	767
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 5 h	 (63)	100
		$SnCl_4$	 (—)	770
		$SnCl_4$, $Cl(CH_2)_2Cl$, 70°, 5 h	 (58) R = 	766
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 5 h	 (41)	100
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (19)	637
		$SnCl_4$, MeCN, −15°, 3 h	 (55) α:β = 3:2	45
C_{16}  R = $CO_2CH_2CCl_3$		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, time	 time: 24 h (90); 2 h (87)	771 722
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, reflux 1.5 h 2. NH_3, MeOH	 (97) R = 	772
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 1.5 h 2. NH_3, MeOH	 (73)	772
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 2 h 2. NH_3, MeOH, rt, 3 h	 (68)	772

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

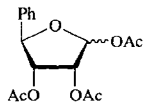
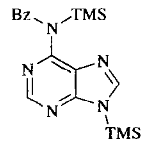
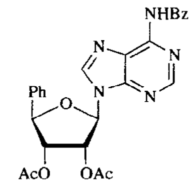
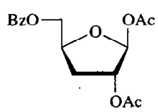
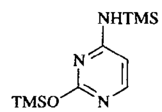
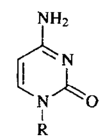
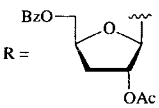
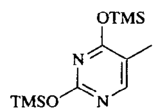
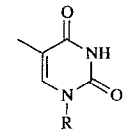
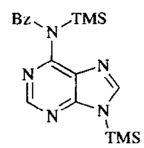
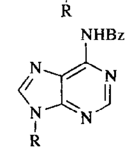
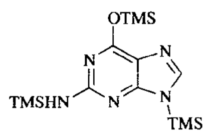
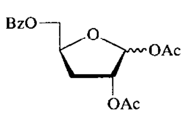
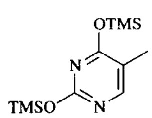
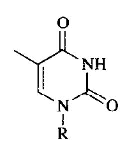
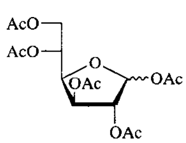
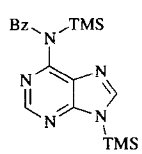
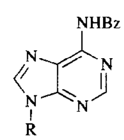
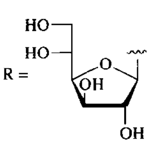
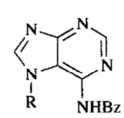
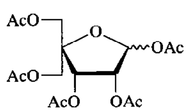
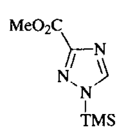
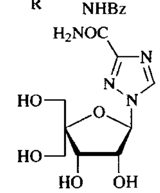
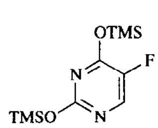
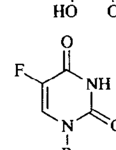
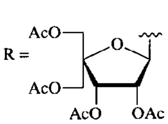
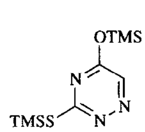
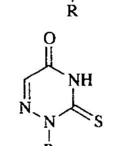
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 1 h	 (80)	579
		$SnCl_4$, MeCN, rt, 45 min - 2 h	 (60) R = 	773
		$SnCl_4$, MeCN, rt, 45 min - 2 h	 (85)	773
		$SnCl_4$, MeCN, rt, 45 min - 2 h	 (55)	773
		$SnCl_4$, MeCN, rt, 45 min - 2 h	N^7 + N^9-β-isomers (57)	773
		$SnCl_4$, MeCN	 (93)	774
		1. $SnCl_4$, (2-3 eq), $Cl(CH_2)_2Cl$, 48-72 h 2. NaOMe, MeOH	 (60-70) R = 	101
		1. $SnCl_4$, (1 eq), $Cl(CH_2)_2Cl$, 48-72 h 2. NaOMe, MeOH	 (60-70)	101
		1. $SnCl_4$, $Hg(CN)_2$, MeCN, 50°, 2 h 2. NH_3, MeOH	 (50)	629
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60°, 1 h	 (84) R = 	629
		$SnCl_4$, MeCN, 55°, 1 h	 (80)	629

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

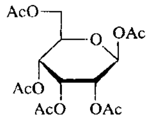
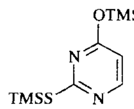
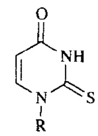
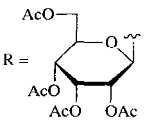
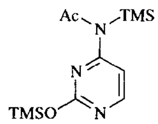
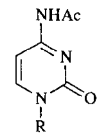
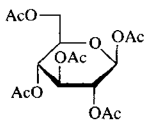
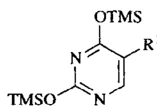
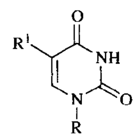
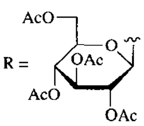
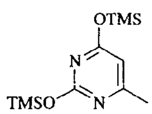
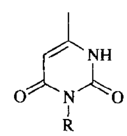
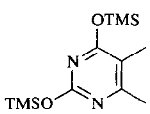
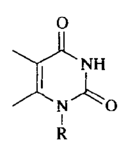
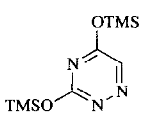
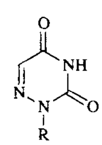
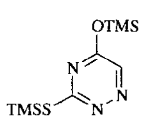
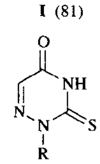
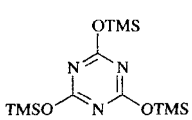
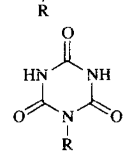
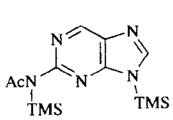
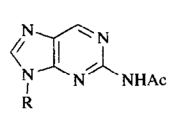
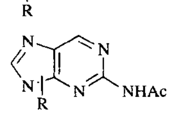
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23°, 12 h	 I (58) + N^3-isomer (34) + N^1,N^3-bis(isomer) (8) R = 	90
		$SnCl_4$, MeCN, 23°, 12 h	I (90) + N^1,N^3-bis(isomer) (6)	90
		$SnCl_4$, $Cl(CH_2)_2Cl$, 22°, 4 h	 (83)	775
		$SnCl_4$	 R = 	
	R^1			
	F	MeCN, <10°, 3 h	(80)	514b
	NO_2	$Cl(CH_2)_2Cl$, 23°, 5 h	(82)	90
		MeCN, 23°, 12 h	(77)	90
	OMe	$Cl(CH_2)_2Cl$, 23°, 3.5 h	(61) + N^3-isomer (25)	90
		MeCN, 23°, 12 h	(83) + N^3-isomer (15)	90
		$SnCl_4$, MeCN, 22°, 3 h	 (42)	89a
		$SnCl_4$, MeCN, 22°, 15 h	 (22)	89a
		$SnCl_4$, $Cl(CH_2)_2Cl$, C_6H_6, 22°, 5 h	 I (62)	84
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23°, 12 h	I (82)	90
		$SnCl_4$, MeCN, 23°, 12 h	I (81)	90
		$SnCl_4$, $Cl(CH_2)_2Cl$, 50°, 3 h	 (79)	84
		$SnCl_4$, $Cl(CH_2)_2Cl$, 45°, 36 h	 I (32)	776
		$SnCl_4$, MeCN, rt, 3 h	 (11)	409
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, reflux, 0.5-1 h	 (78) N^9:N^7 = 98:2	409

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

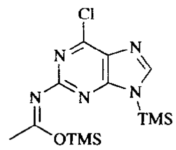
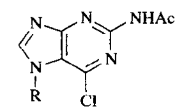
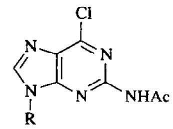
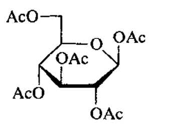
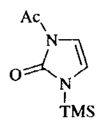
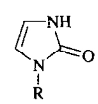
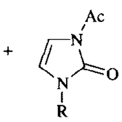
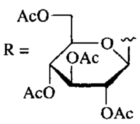
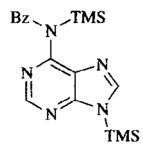
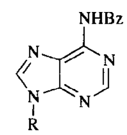
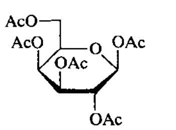
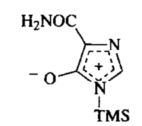
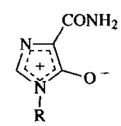
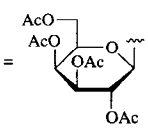
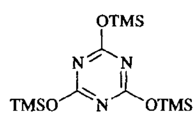
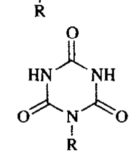
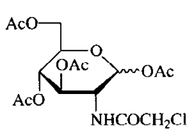
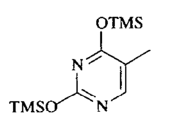
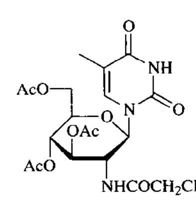
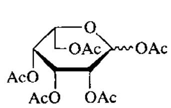
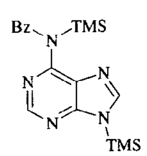
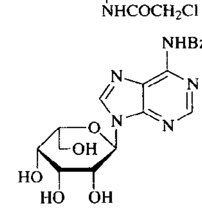
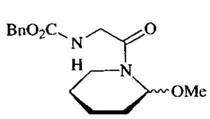
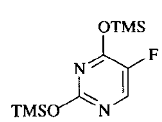
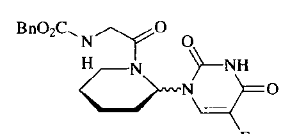
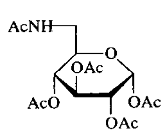
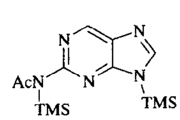
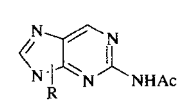
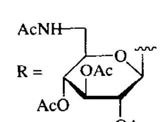
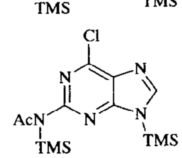
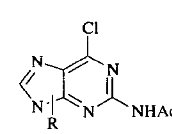
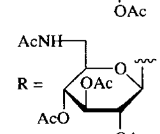
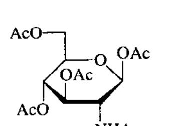
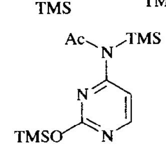
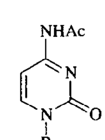
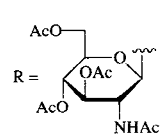
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, rt, 16 h	 (59) + N^9-isomer (7)	409
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, reflux, 1 h	 (33) + N^7-isomer (33)	409
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 18 h	 (32) +  (12) R = 	777
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 5 h	 (68)	100
		$SnCl_4$, TMSTf, CH_2Cl_2, reflux, 2 h	 (—) R = 	778
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23°, 40 h	 (60) + N^1,N^3-bis(riboside) (16)	745
		$SnCl_4$, $Cl(CH_2)_2Cl$, MS 4 Å	 (64)	779
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 5 h 2. NaOMe, MeOH	 (68)	780
		$SnCl_4$, MeCN, –40 to –45°, 10 min	 (40)	642
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, 135°, 0.5-1 h	 (67) N^9:N^7 = 98:2 R = 	409
		$SnCl_4$, MeCN, rt, 3 h	 (22) N^9:N^7 = 59:41 R = 	409
		$SnCl_4$, $Cl(CH_2)_2Cl$, 70°, 5 h	 (71) R = 	766

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

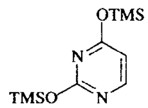
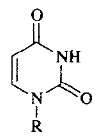
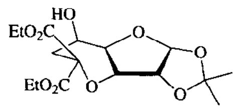
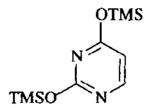
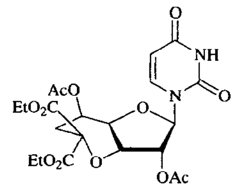
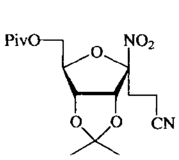
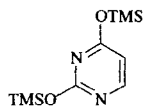
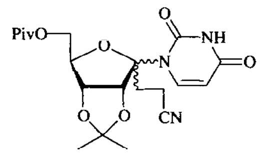
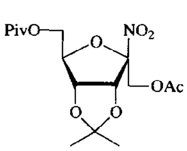
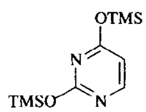
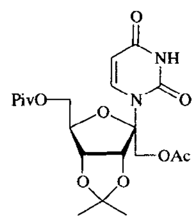
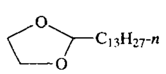
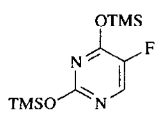
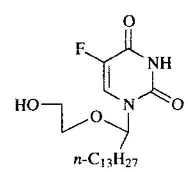
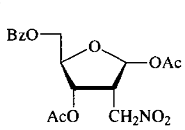
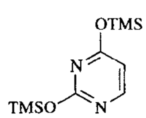
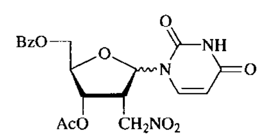
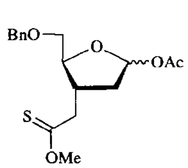
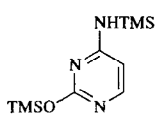
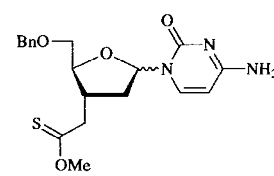
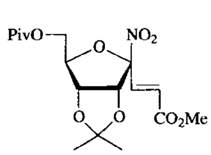
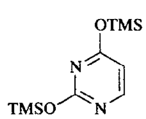
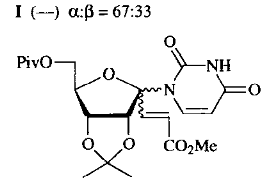
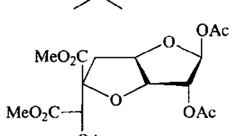
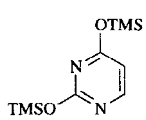
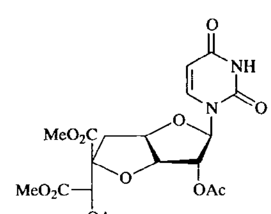
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, 70°, 5 h	 (50)	766
		1. $SnCl_4$ 2. Ac_2O	 (—)	781
		$SnCl_4$, MeCN, −30°, 20 min	 (40) α:β = 2:3	106
		$SnCl_4$, MeCN, 65°, 30 min	 (15)	106
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (14)	637
C_{17} 		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 4 h	 (—) α:β = 10:1	217
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt	 I (—) α:β = 9:91	278
		$SnCl_4$, MeCN, rt	I (—) α:β = 67:33	278
		$SnCl_4$, MeCN, 0°, 1 h	 (30) α:β = 1:1.2	106
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0°, 12 h	 (83)	782

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

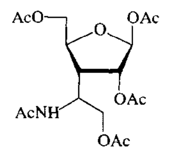
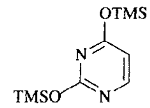
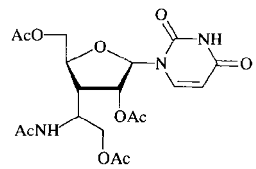
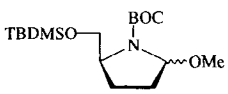
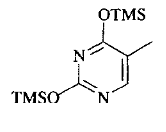
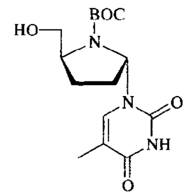
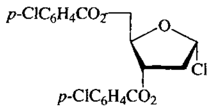
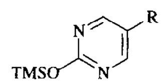
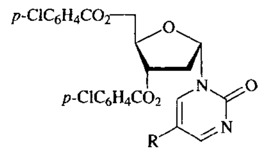
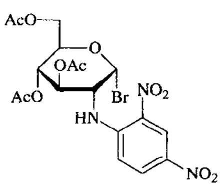
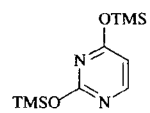
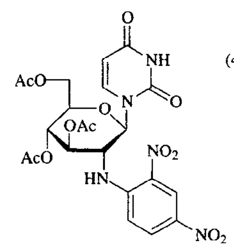
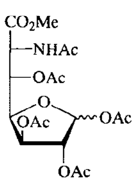
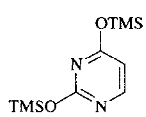
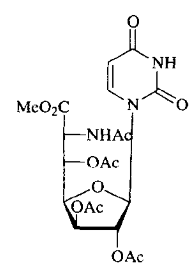
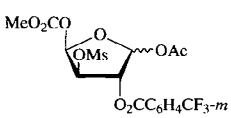
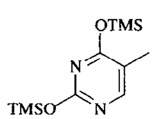
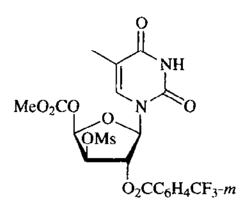
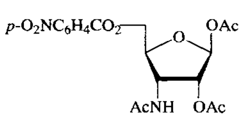
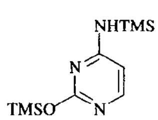
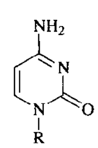
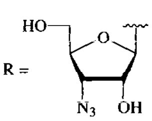
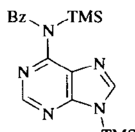
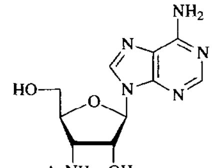
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 4 h	 (51) α:β = 2:1	216
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 0-20° 2. TBAF, THF, 0°	 (77) α:β = 9:1	783
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0°, 2-2.5 h	 R / I (20) β-anomer (20) / C≡CH (14) β-anomer (12)	784
C_{18} 		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 4 h	 (45)	218
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 21 h	 (92)	785
		$SnCl_4$, CH_2Cl_2, rt, 20 h	 (52)	545
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, reflux, 1.5 h 2. NH_4OH (10%), rt, 12 h	 (60) R = 	772
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, reflux, 8 h 2. NH_3, MeOH, rt, 30 h	 (64)	772

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

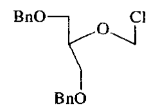
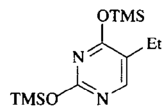
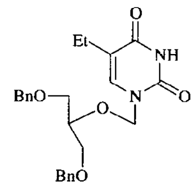
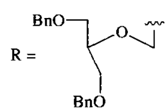
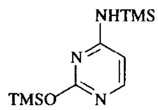
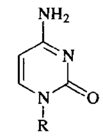
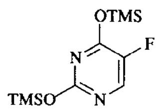
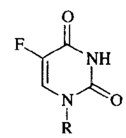
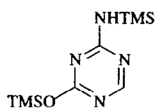
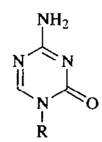
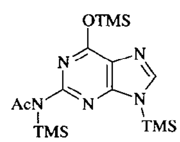
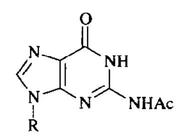
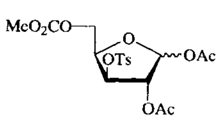
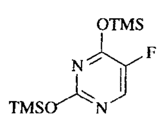
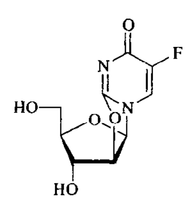
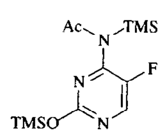
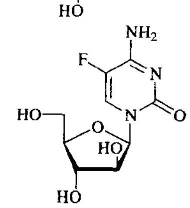
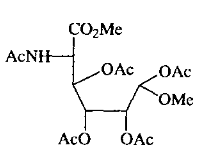
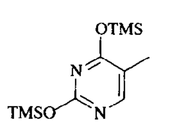
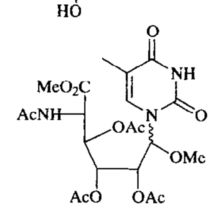
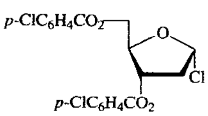
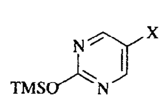
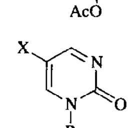
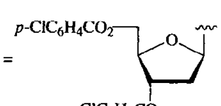
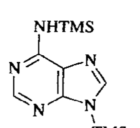
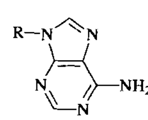
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, rt, 48 h	 (100) R = 	654
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12-14 h	 (34)	786, 787
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (88)	787
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12-14 h	 (39)	786, 787
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (9) + N^7-isomer (3)	788
		1. $SnCl_4$, MeCN, rt, 3 h 2. NaOMe, MeOH	 (70)	514b
		1. $SnCl_4$, MeCN, rt, 2.5 h 2. OH^-	 (47)	514b
		$SnCl_4$, $Cl(CH_2)_2Cl$, 95°, 1 h	 (67)	789
C_{19} 		$SnCl_4$, $Cl(CH_2)_2Cl$, 0°	 R = 	681
	X		α-anomer	
	Br	15 min	(9) (8)	
	I	2.5 h	(20) (20)	
		$SnCl_4$, $C_6H_3Cl_3$-1,4,5, rt, 18 h	 (27) α:β = 51:49	790

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

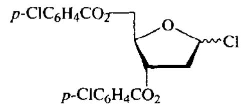
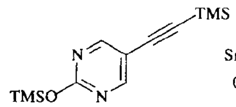
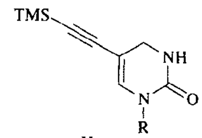
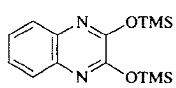
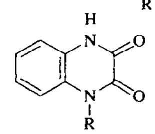
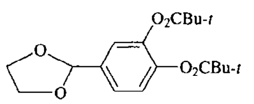
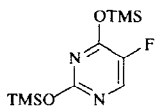
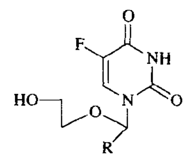
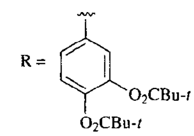
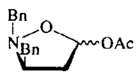
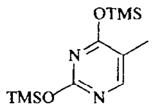
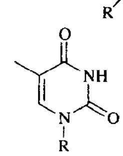
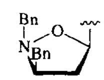
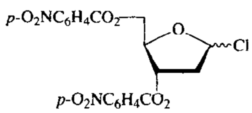
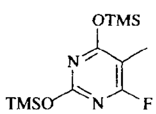
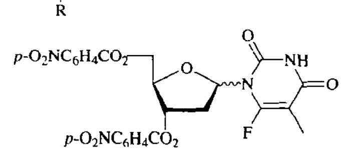
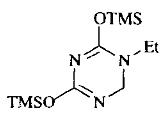
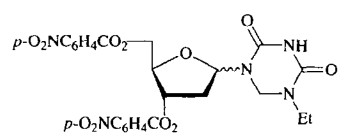
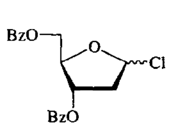
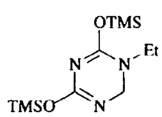
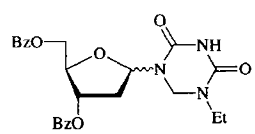
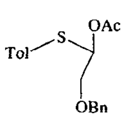
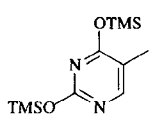
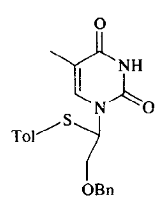
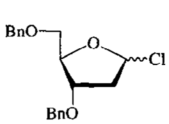
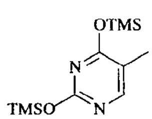
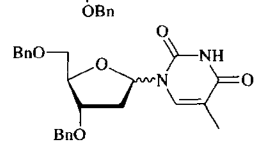
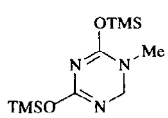
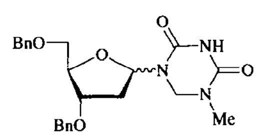
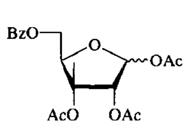
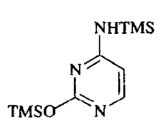
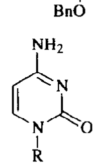
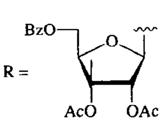
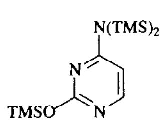
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0°, 2 h	 (14) + α-anomer (12)	791
		$SnCl_4$, CH_2Cl_2, rt, 16 h	 (13) + α-anomer (5)	657
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (40) R = 	637
		$SnCl_4$, CH_2Cl_2, 0°	 (90) α:β = 3:2 R = 	792
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0°, 24 h	 (—)	721
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, –25°, 5 min 2. 20°, 25 min	 (—)	669
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, –25°, 5 min 2. 20°, 25 min	 (—)	669
		$SnCl_4$, CH_2Cl_2, rt, 18 h	 (84)	793
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 2 h	 (30) α:β = 3:2	794
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 2 h	 (14) α:β = 1:1	794
		$SnCl_4$, MeCN	 I (—) R = 	795
		$SnCl_4$, MeCN, 20°, 16 h	I (68)	796

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

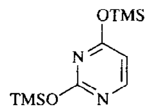
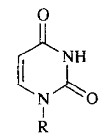
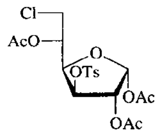
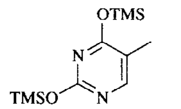
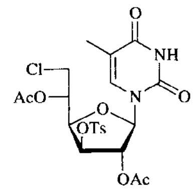
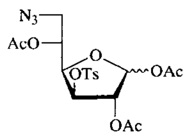
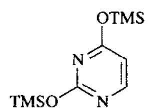
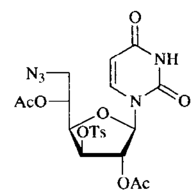
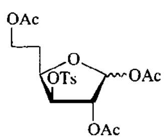
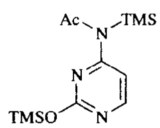
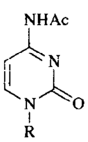
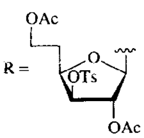
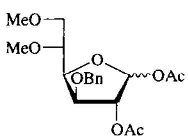
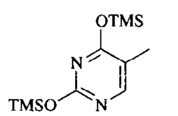
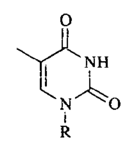
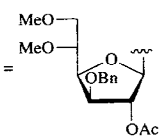
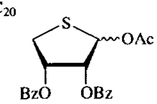
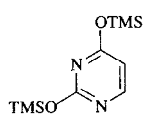
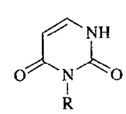
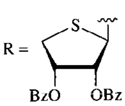
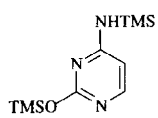
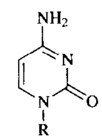
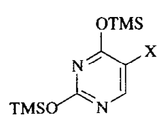
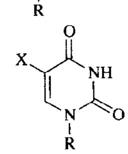
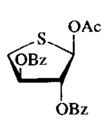
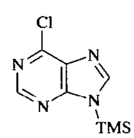
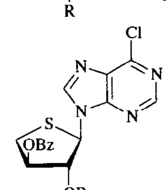
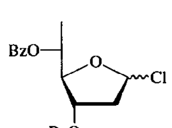
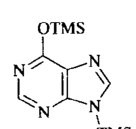
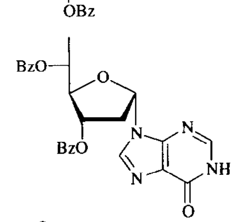
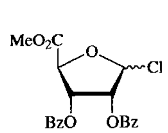
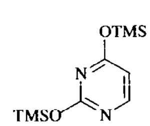
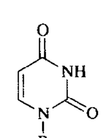
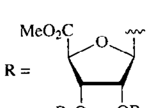
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, 20°, 16 h	 (80) + N^3-isomer (7)	796
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 3 h	 (37)	797
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 6 h	 (42) + α-anomer (15)	797
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (46) R = 	798
		$SnCl_4$, CH_2Cl_2, rt, 18 h	 (85) R = 	742
C_{20} 		$SnCl_4$, CH_2Cl_2, rt, 12 h, or $SnCl_4$	 (35) R = 	686, 687
		$SnCl_4$	 (61)	686
		$SnCl_4$	 X: F (—) + N^3-isomer (—); I (—)	686
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (14)	687
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (6) + mixture of nucleoside isomers (38)	527
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60°, 4 h	 (47) + N^3-β-isomer (20) R = 	224

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

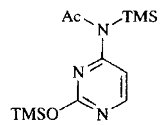
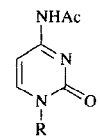
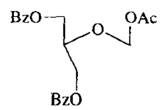
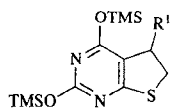
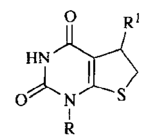
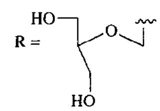
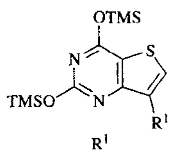
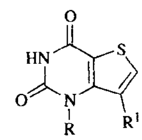
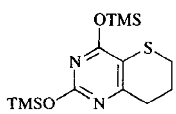
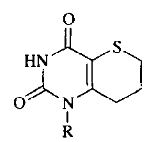
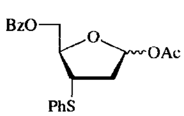
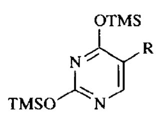
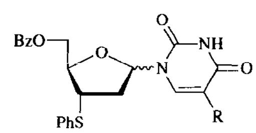
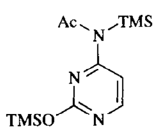
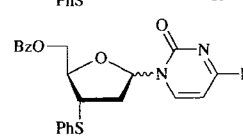
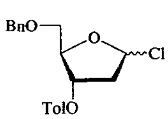
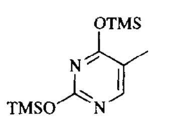
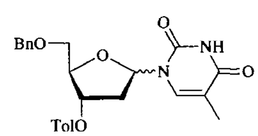
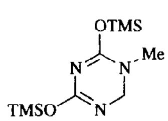
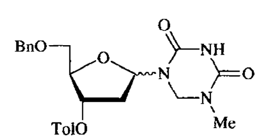
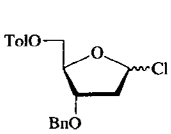
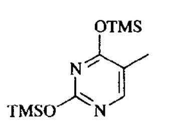
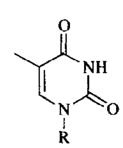
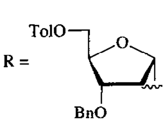
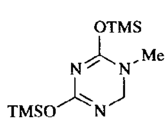
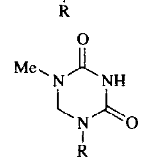
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, 25°, 20 h	 (82)	224
		1. $SnCl_4$, CH_2Cl_2, rt, 18 h 2. NH_3, MeOH	 R^1: H (35), Ph (15); R = 	658
		1. $SnCl_4$,$Cl(CH_2)_2Cl$, −30°, 18 h 2. NH_3, MeOH		659
	R^1			
	p-FC_6H_4		(31)	
	p-ClC_6H_4		(24)	
	p-BrC_6H_4		(35) + N^3-isomer (15)	
	Me		(63)	
	Ph		(43)	
	Tol		(32)	
	p-$MeOC_6H_4$		(64)	
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 24°, 18 h 2. NH_3, MeOH	 (20)	658
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 R: H (73) α:β 31:69; Me (34) α:β 52:48	229
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (89) α:β = 43:57	229
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 2 h	 (15) α:β = 1::2	794
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 2 h	 (20) α:β = 1:1	794
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 2 h	 (3) R = 	794
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 2 h	 (11)	794

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

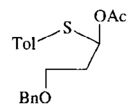
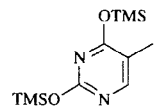
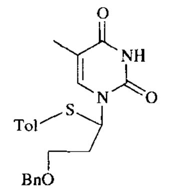
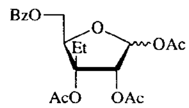
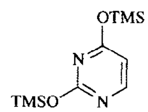
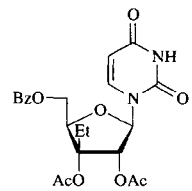
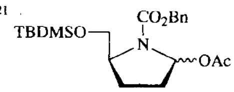
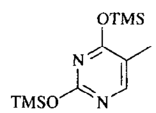
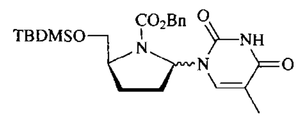
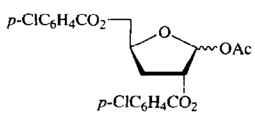
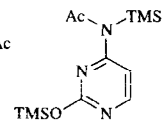
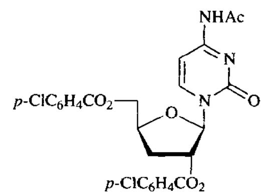
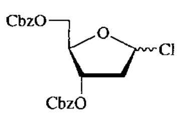
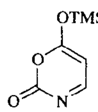
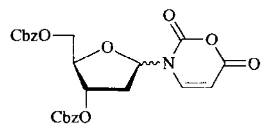
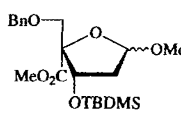
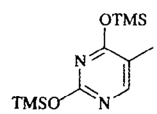
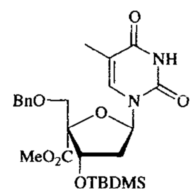
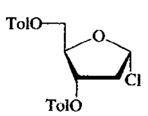
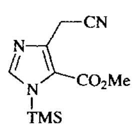
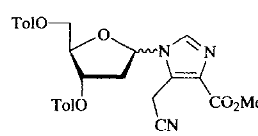
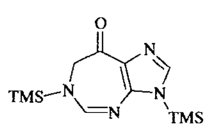
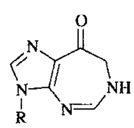
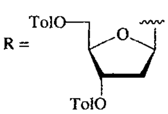
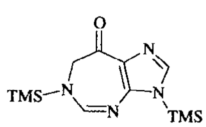
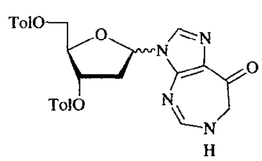
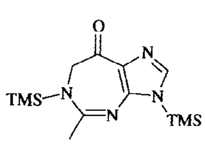
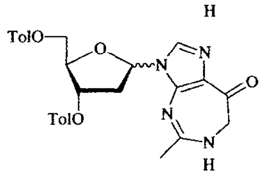
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$ (3 eq), CH_2Cl_2, rt, 3 h	 (52)	793
		$SnCl_4$, MeCN	 (—)	795
C_{21} 		$SnCl_4$, CH_2Cl_2, −15°, 3 h	 (64)	45
		$SnCl_4$, MeCN, rt, 12 h	 (100)	800
		$SnCl_4$, C_6H_6	 (15) α:β = 1:1	801
		$SnCl_4$, MeCN	 (35) + α-anomer (35)	802
		$SnCl_4$, $Cl(CH_2)_2Cl$	 rt, 18 h (>70) 35°, 2 h (85) α:β = 80:20	803
		$SnCl_4$, Py, $Cl(CH_2)_2Cl$, MeCN, −35°, 45 min	 (30) + α-anomer (32) R = 	557
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, Cond.	 Cond. α:β −20°, 1.5 h 60:40 (89) −35°, 0.75 h 50:50 (62)	804 805
		$Cl(CH_2)_2Cl$, MeCN 1. 50-60°, 2 h 2. $SnCl_4$, −20°, 1.5 h	 I (—) α:β = 40:60	804
		Py, MeCN 1. 50-60°, 2 h 2. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, −35°, 45 min	I (89) α:β = 2:3	557

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

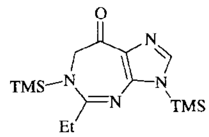
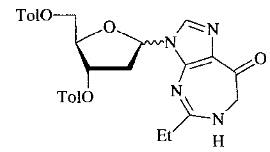
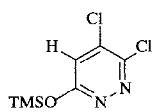
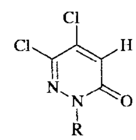
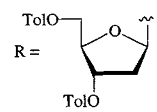
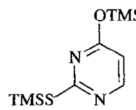
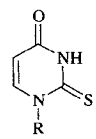
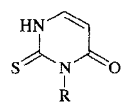
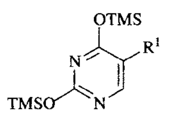
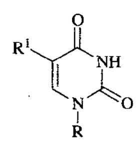
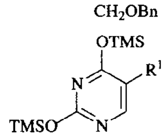
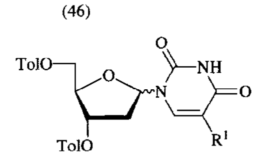
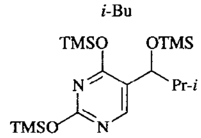
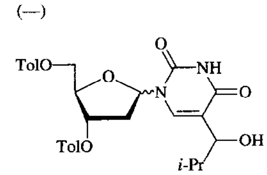
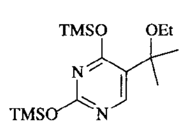
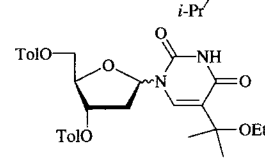
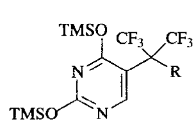
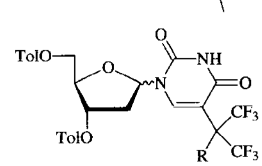
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, $Cl(CH_2)_2Cl$, −35°, 45 min	 (89) α:β = 2:3	557
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0-5°, 2 h	 (57) + α-anomer (20) R = 	524
		$SnCl_4$, $Cl(CH_2)_2Cl$ −40°, 6.5 h	 (94)	494
		$SnCl_4$, CH_2Cl_2, −78°, 5 h	 (25)	494
		$SnCl_4$, $Cl(CH_2)_2Cl$		
	R^1			
	TMS	20-22°, 4 h	(51)	806
	Et	0°, 2 h	(57)	84
	$CH=CH_2$	0-5°, 2-3 h, rt, 8-10 h	(30) + α-anomer (9)	807
	$CH=CH_2$	C_6H_6, rt, 8-10 h	(30) + α-anomer (9)	808
	CH_2OBn	rt, 2 h	(46)	809
		$SnCl_4$, $Cl(CH_2)_2Cl$		
	R^1			
	Me	MeCN, rt, 2 h	(65) α:β = 1:3	794
	i-Pr	MeCN (no $Cl(CH_2)_2Cl$), 0-4°, 18 h	(70) α:β = 1:10	810
	s-Bu	—	(—)	718
	i-Bu	—	(—)	718
		$SnCl_4$, $Cl(CH_2)_2Cl$	 (—)	718
		$SnCl_4$, $Cl(CH_2)_2Cl$	 (—)	718
		$SnCl_4$, $Cl(CH_2)_2Cl$	 R: F (—); OH (—)	718

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

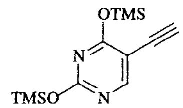
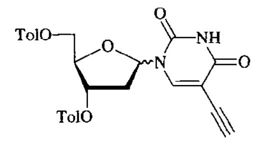
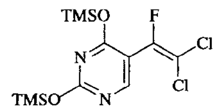
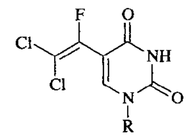
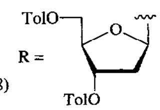
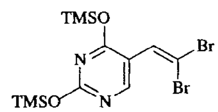
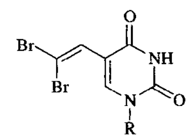
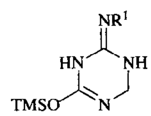
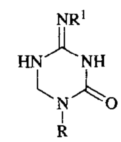
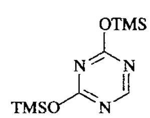
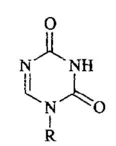
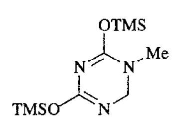
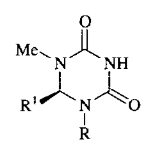
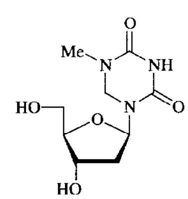
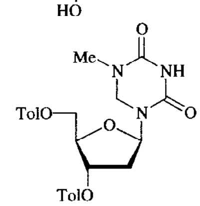
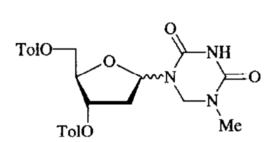
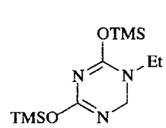
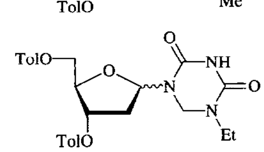
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $SnCl_4$, CH_2Cl_2, 0°, 8 h 2. 20°, 18 h	 (85) α:β = 6:5	813
		1. $SnCl_4$, CH_2Cl_2, 0°, 8 h 2. 20°, 24 h	 (30) + α-anomer (28) R = 	812
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0-5°	 (71) α:β = 1:3	813
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, −25°, 5 min 2. 20°, 25 min	 R^1: H (—); Ac (—)	669
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, −25°, 5 min 2. 20°, 25 min	 (—)	669
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 18 h 2. R^1MgBr	 R^1: Me (43); Ph (54)	512
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. $NaBH_4$ 3. OH^-	 (13) + α-anomer (12)	512
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 3-5 h 1. −20°, 5 min 2. 25°, 3-5 h	 **I** (23)	239
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, −25°, 5 min 2. 20°, 25 min	**I** (29)	669
		1. $SnCl_4$, MeCN, −20°, 5 min 2. 25°, 3-5 h	 **II** (57) α:β = 1:1	239
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, −25°, 5 min 2. 20°, 25 min	 (—)	669

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

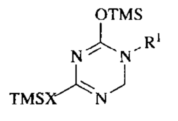
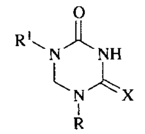
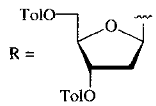
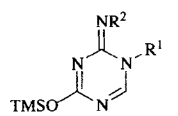
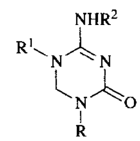
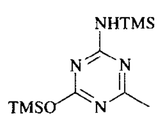
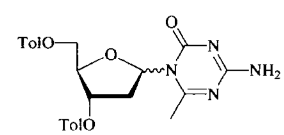
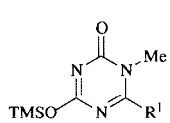
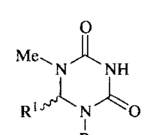
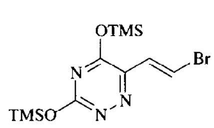
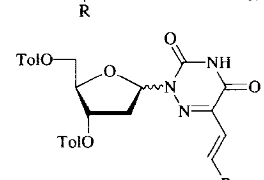
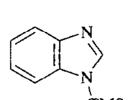
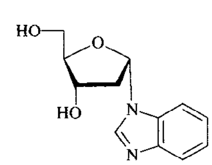
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, –25°, 5 min 2. 20°, 25 min	 R = 	669
	X / R^1			
	O / *n*-Pr		(—)	
	O / *n*-Bu		(—)	
	O / *i*-Pr		(—)	
	O / $MeOCH_2$		(—)	
	O / $MeSCH_2$		(—)	
	O / *c*-C_3H_5		(—)	
	S / Me		(—)	
	S / Et		(—)	
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, –25°, 5 min 2. 20°, 25 min		669
	R^1 / R^2			
	Me / H		(—)	
	Et / H		(—)	
	n-Pr / H		(—)	
	i-Pr / H		(—)	
	c-C_3H_5 / H		(—)	
	Me / Ac		(—)	
	Et / Ac		(—)	
	n-Pr / Ac		(—)	
	i-Pr / Ac		(—)	
	c-C_3H_5 / Ac		(—)	
		$SnCl_4$ (1.37 eq), MeCN, 0°, 40 min	 **I** (40) $\alpha:\beta$ = 1:1.3	814
		$SnCl_4$ (1.46 eq), $MeCN/Cl(CH_2)_2Cl$ (2:5), 20°, 135 min	**I** (25) $\alpha:\beta$ = 1:1.8	814
		$SnCl_4$ (0.68 eq), MeCN, 20°, 125 min	**I** (30) $\alpha:\beta$ = 1:2.4	814
		$SnCl_4$ (0.68 eq), $Cl(CH_2)_2Cl$, 20°, 1 h	**I** (46) $\alpha:\beta$ = 1:2.5	814
		$SnCl_4$ (0.68 eq), $Cl(CH_2)_2Cl$, 20°, 85 min	**I** (45) $\alpha:\beta$ = 1:2.6	814
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 4 h	 R^1: Me (21) + α-anomer (9); Ph (21) + α-anomer (9) + N^3-α- and N^3-β-isomers (20)	512
		$SnCl_4$, $Cl(CH_2)_2Cl$, 25°	 (34) $\alpha:\beta$ = 3:3.2	815, 546
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 0°, 105 min 2. NaOMe, MeOH	 (33) + β-anomer (10)	816

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

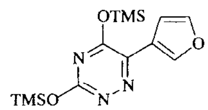
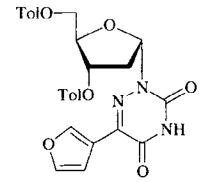
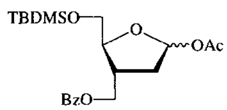
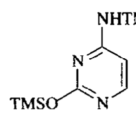
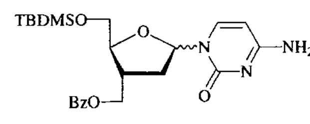
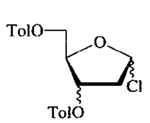
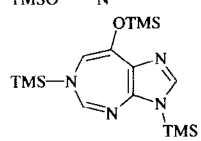
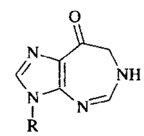
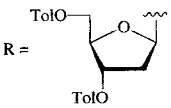
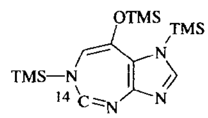
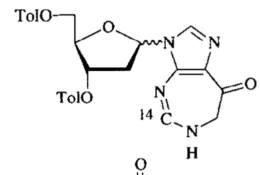
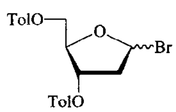
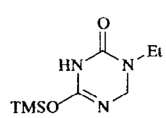
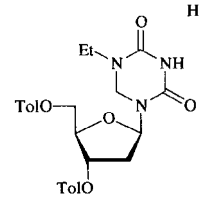
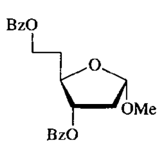
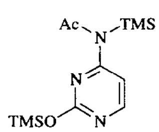
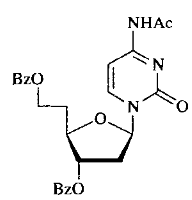
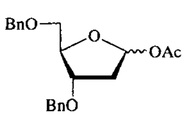
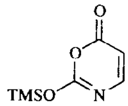
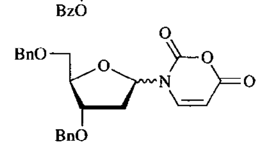
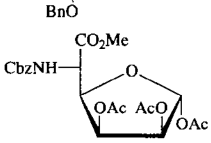
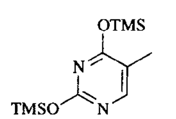
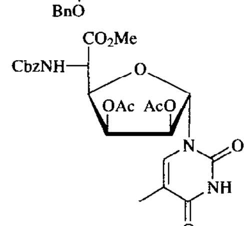
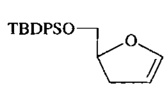
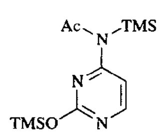
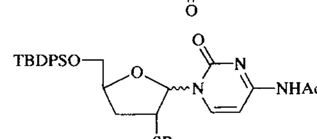
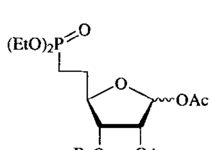
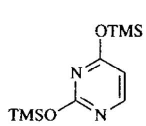
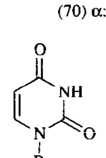
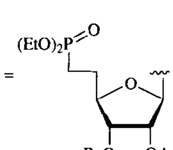
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 2.5 h	 (33)	546
		$SnCl_4$	 (—) α:β = 1:1	817
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, –35°, 45 min	 (35) + α-anomer (17) R = 	818
		$SnCl_4$, $Cl(CH_2)_2Cl$/MeCN, (1:1), –35°	 (26)	819
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, –25°, 5 min 2. 20°, 25 min	 (—)	669
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 12 h	 (28)	820
		$SnCl_4$, $Cl(CH_2)_2Cl$, –5 to 0°	 (25) α:β = 1:2	801
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt	 (44)	789
		$SnCl_4$, RSCl, CH_2Cl_2, –78 to 25°, 2 h R: Ph Tipp	 (65) α:β = 1:18 (70) α:β = 1:23	421a
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, 20°, 16 h	 (83) R = 	821

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

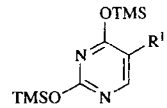
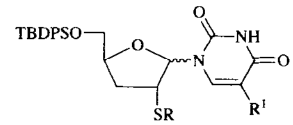
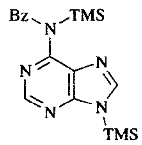
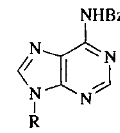
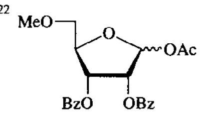
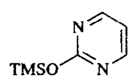
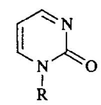
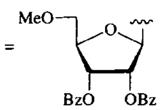
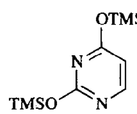
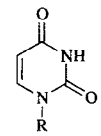
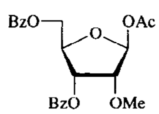
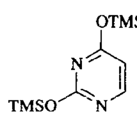
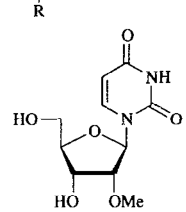
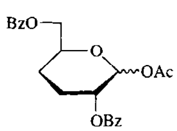
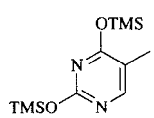
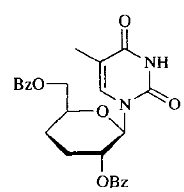
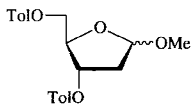
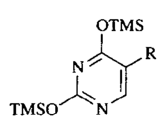
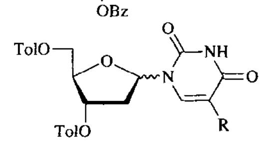
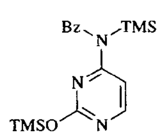
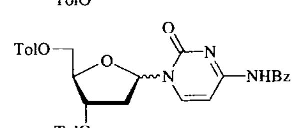
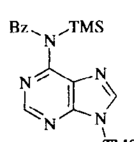
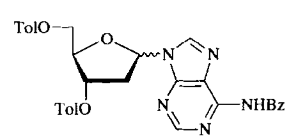
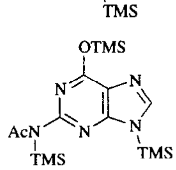
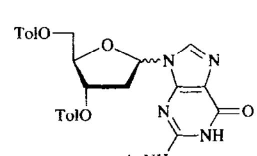
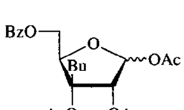
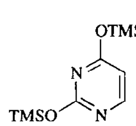
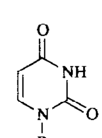
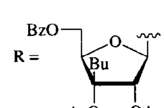
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, RSCl, CH_2Cl_2, −78 to 25°, 2 h		421a
	R^1	R		
	H	Tipp	(52) α:β = 1:99	
	Me	Ph	(68) α:β = 1:42	
	Me	Tipp	(60) α:β = 1:44	
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 16 h	 (80)	821
C_{22} 		$SnCl_4$, MeCN, rt, 2 d	 (45) R = 	822
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 16 h	 (86)	822
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 20°, 16 h 2. NaOMe, MeOH, reflux, 24 h	 (24) + N^3-isomer (16)	225
		$SnCl_4$, MeCN, 40°, 1.5 h	 (88)	823
		$SnCl_4$, MeCN, rt	 R: H (95) α:β = 46:54; Me (97) α:β = 55:45	370b
		$SnCl_4$, MeCN, rt	 (95) α:β = 42:58	370b
		$SnCl_4$, MeCN, rt	 (92) α:β = 75:25	370b
		$SnCl_4$, MeCN, rt	 (75) α:β = 65:35	370b
		$SnCl_4$, MeCN	 (—) R = 	795

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

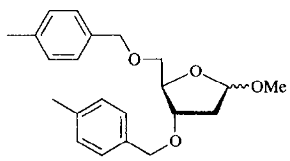
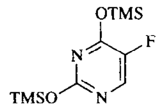
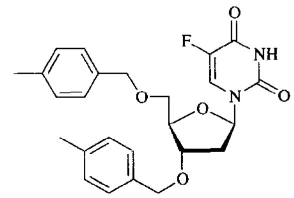
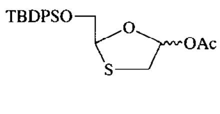
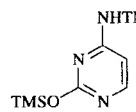
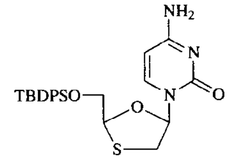
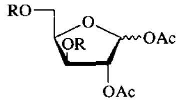
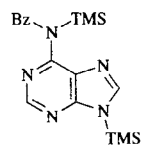
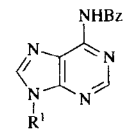
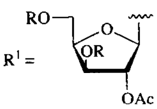
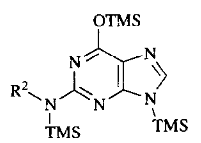
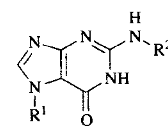
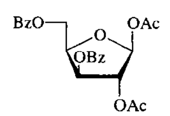
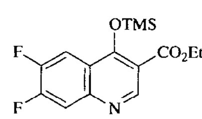
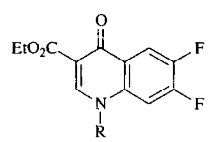
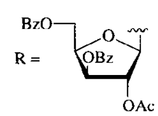
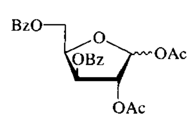
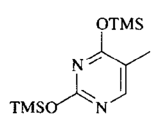
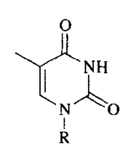
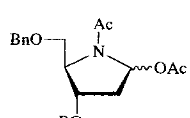
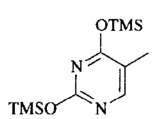
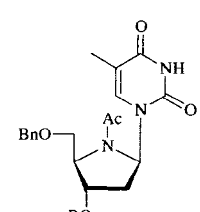
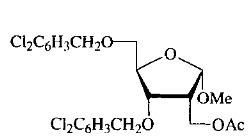
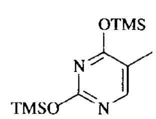
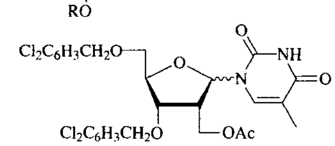
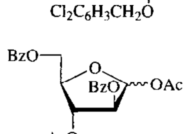
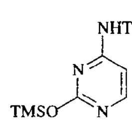
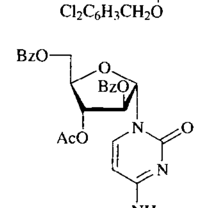
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $SnCl_4$, MeCN, rt, 1 h 2. MeOH	 (11)	824
		$SnCl_4$, MeCN, rt	 (80)	235
C_{23}  R = p-$O_2NC_6H_4CO$		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h	 (90) R^1 = 	825
	 R^2 = n-$C_{11}H_{23}CO$	$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 **I** (37) + N^9-β-isomer (6)	825
		$SnCl_4$, $HgBr_2$, C_6H_6, reflux, 6 h	**I** (44) + N^9-β-isomer (20)	825
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°	 (61) R = 	826
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h 2. $SOCl_2$, MeCN, reflux, 90 min	 **I** (53)	827
		$SnCl_4$, MeCN, reflux, 5 h	**I** (32)	828
		$SnCl_4$, MeCN	 R Bz −15°, 1 h (93) Bn −30°, 3 h (72) α:β = 1:2	45b 45a
		$SnCl_4$, MeCN, 50°	 (66) α:β = 2:98	829
		$SnCl_4$, MeCN, rt	 (93)	830

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

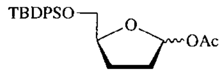
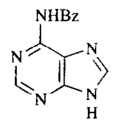
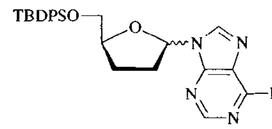
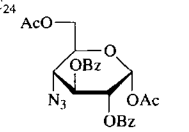
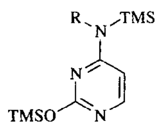
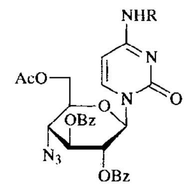
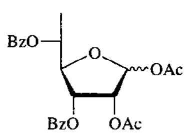
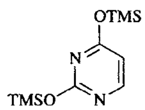
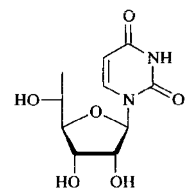
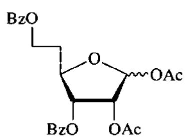
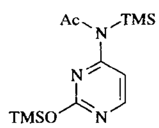
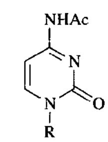
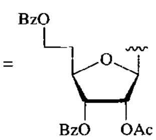
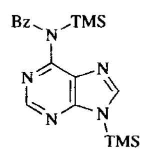
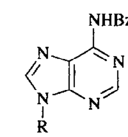
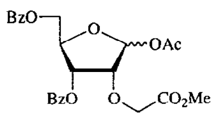
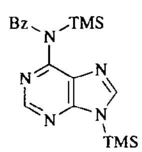
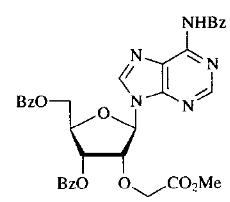
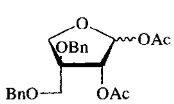
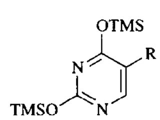
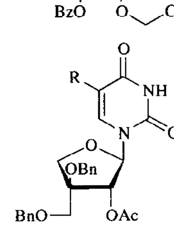
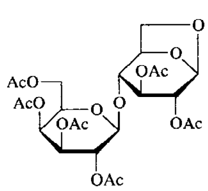
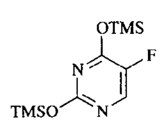
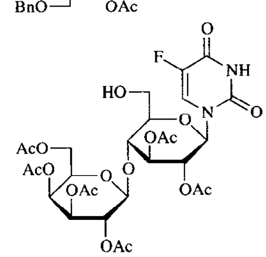
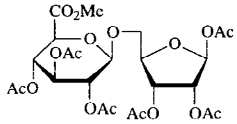
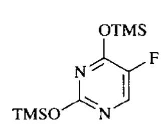
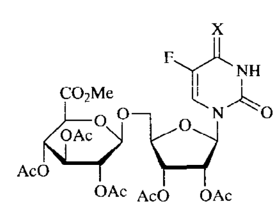
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, -5°	 (—)	831
C_{24} 		$SnCl_4$, $Cl(CH_2)_2Cl$, 50°, 1 h	 R: Ac (85); Bz (76)	832
		1. $SnCl_4$, MeCN, rt, 24 h 2. NH_3, MeOH, rt, 5 d	 (16)	833
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (49) R = 	820, 834
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 16 h	 (72)	821
		$SnCl_4$, MeCN, rt, 3 d	 (63) + α-anomer (14)	835
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt	 R: H 18 h (85); Me 13 h (81)	672
		$SnCl_4$, reflux, 5 h	 I (—)	836
		$SnCl_4$, MeCN, reflux, 10 h	I (35)	692
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 30 min	 I, X = O (92)	837

TABLE LII. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

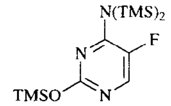
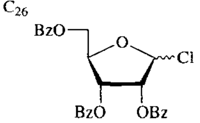
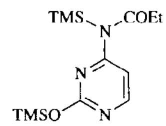
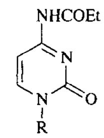
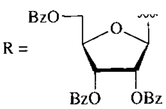
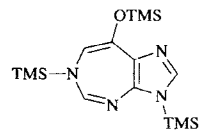
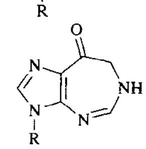
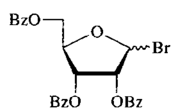
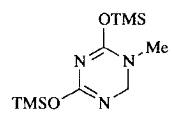
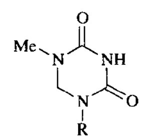
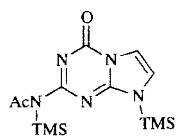
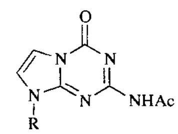
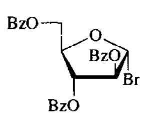
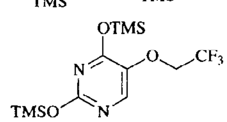
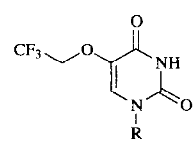
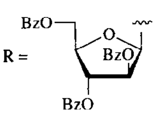
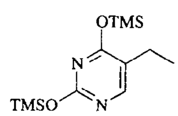
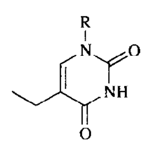
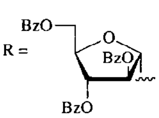
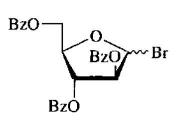
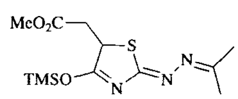
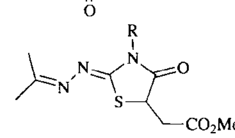
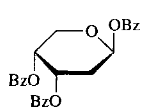
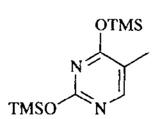
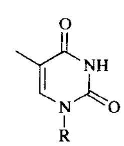
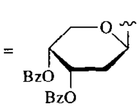
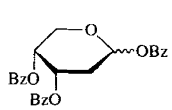
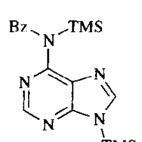
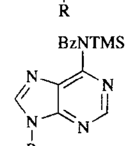
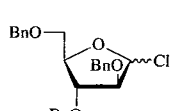
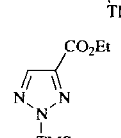
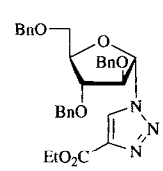
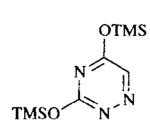
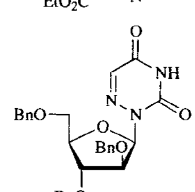
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 35 min	I, X = NH (98)	837
C_{26} 		$SnCl_4$, $Cl(CH_2)_2Cl$, 50°, 5 h	 (—) R = 	424a
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, −35°, 45 min	 I (51)	557, 818
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 48 h	 (21)	239
		$SnCl_4$, MeCN	 (—)	838
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (57) R = 	369
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 (82) R = 	358
		1. $SnCl_4$, MeCN, 0°, 10 min 2. 90°, 2 h	 (31)	839
		$SnCl_4$, $Cl(CH_2)_2Cl$, 20°	 (36) R = 	840
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 6 h	 (28) + α-anomer (24)	841
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (20) + β-anomer (17) + N^3-α-isomer (15) + N^2-β-isomer (10) + N^2-α-isomer (17)	842
		$SnCl_4$, $Cl(CH_2)_2Cl$, 22°, 16 h	 (42)	84

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

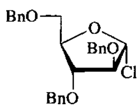
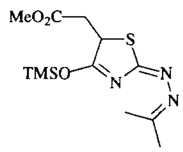
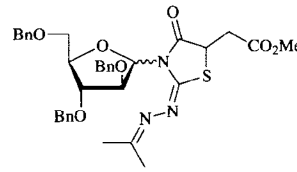
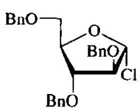
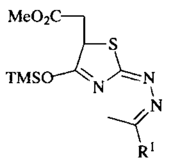
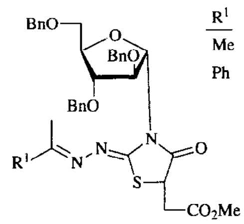
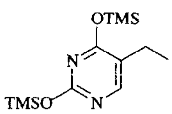
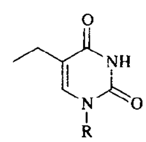
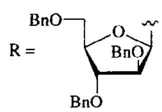
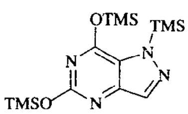
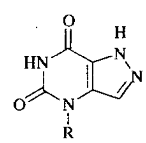
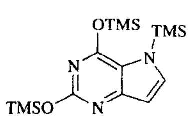
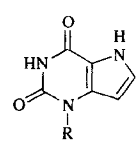
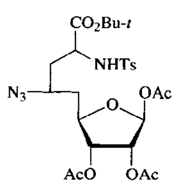
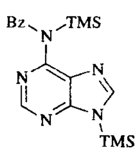
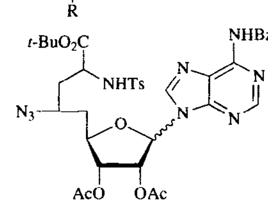
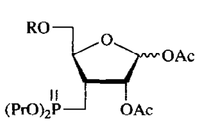
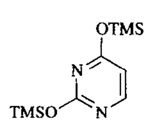
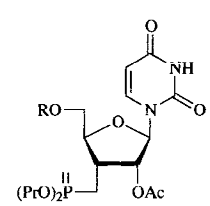
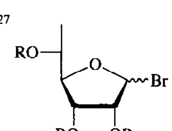
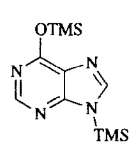
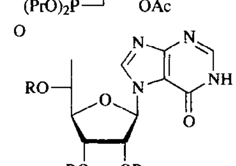
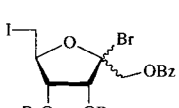
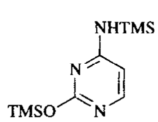
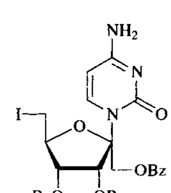
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, rt, 12 h		839
		C_6H_6	(40) α:β = 4:1	
		$Cl(CH_2)_2Cl$	(45) α:β = 6:1	
		$SnCl_4$ A. CH_2Cl_2, rt, 12 h B. $Cl(CH_2)_2Cl$, 0°, 30 min; rt, 12 h	 R^1 Me: A. (35) + β-anomer (6) R^1 Ph: B. (53) + β-anomer (6)	839
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 16 h	 (85) α,β mixture R = 	358
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (29) + N^1-isomer (7)	362
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (42) + N^5-isomer (15)	362
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, 22°, 16 h	 (50)	192g
 R = $CO(CH_2)_2COPh$		$SnCl_4$, MeCN, rt, 24 h	 (80)	843
C_{27}  R = p-$O_2NC_6H_4CO$		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (20)	844
		$SnCl_4$, $Hg(CN)_2$, C_6H_6, 60°, 1.5 h	 (56)	632

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

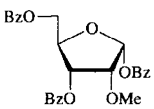
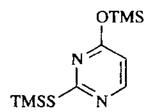
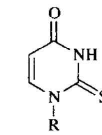
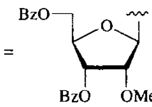
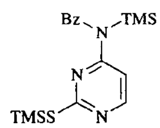
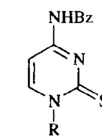
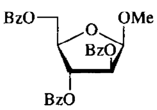
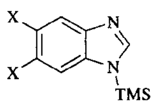
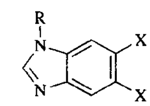
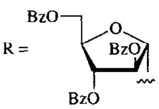
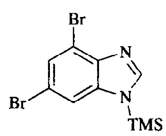
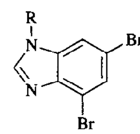
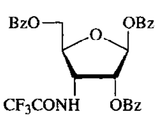
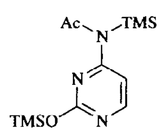
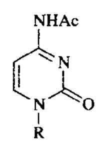
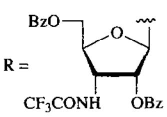
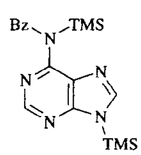
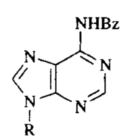
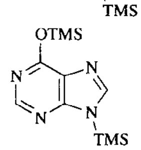
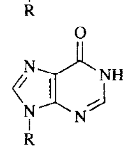
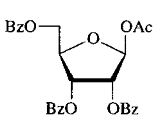
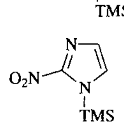
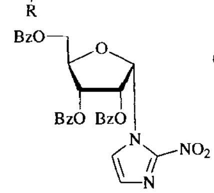
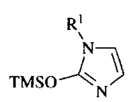
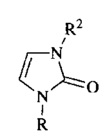
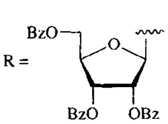
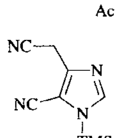
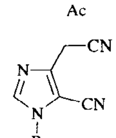
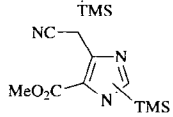
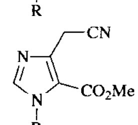
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, rt, 3 h	 (39) R = 	845
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux	 (70)	846, 847
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 30 min	 I X = H (18) R = 	848
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 26 h, reflux, 15 min	I X = Cl (24)	848
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 6 h, rt, 12 h	 (35) + isomer	849
C_{28} 		$SnCl_4$, $Cl(CH_2)_2Cl$, 25°, 16 h	 (69) R = 	766
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 5 h	 (61)	100
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 5 h	 (67)	100
		$SnCl_4$, MeCN, 60°, 1 h	 (38)	213
		$SnCl_4$, $Cl(CH_2)_2Cl$	 R = 	
	R^1		R^2	
	TMS	0°, 5 h	H (19)	850
	Ac	20°, 6 h	Ac (51)	777
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 5.5 h	 (72) + N^3-isomer (18)	851
		$SnCl_4$ (0.72 eq), $Cl(CH_2)_2Cl$, rt, 9 h	 (35)	704

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

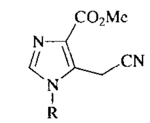
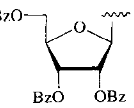
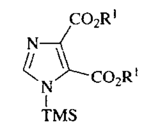
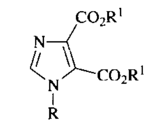
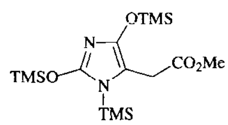
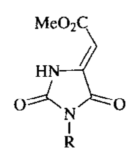
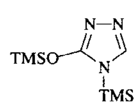
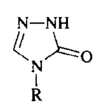
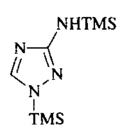
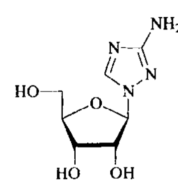
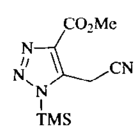
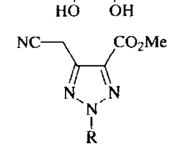
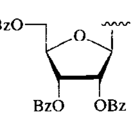
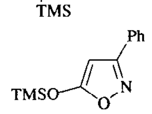
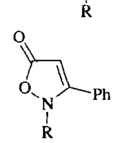
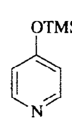
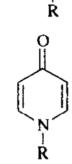
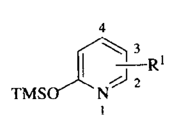
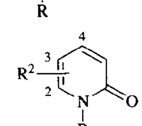
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 **I** (100) R = 	704
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 6 h	**I** (50) + N^3-β-isomer (10)	704
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 48 h	 **I**, R^1 = Me, (82)	852
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 2 d	**I**, R^1 = Me, (78)	853
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt,15 min	**I**, R^1 = Me, (90)	543
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 48 h	**I**, R^1 = Et, (84)	852
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 2 d	**I**, R^1 = Et, (—)	853
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 2 d	 (80)	720
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, rt, 5 h	 (21) + α-anomer (1) + N^2,N^4-bis(riboside) (29)	850
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 3.5 h 2. NH_3, MeOH, rt, 4 d	 (—) + N^2-isomer (—) + N^4-isomer (—)	854
		$SnCl_4$ (0.72 eq), $Cl(CH_2)_2Cl$, rt, 25 h	 (94) R = 	855
		$SnCl_4$	 (—)	856
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 1 h	 (63) + *O*-riboside (2)	99
		$SnCl_4$, $Cl(CH_2)_2Cl$		
	R^1		R^2	
	H	rt, 12 h	H (85)	99, 388
	4-NHTMS	rt, 8 h	4-NH_2 (97)	856
	3-NO_2	reflux, 8 h	3-NO_2 (72)	714

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

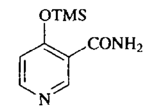
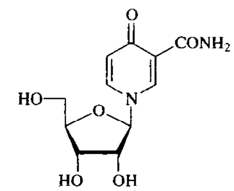
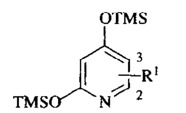
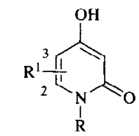
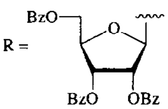
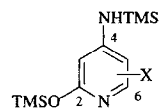
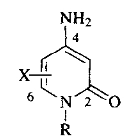
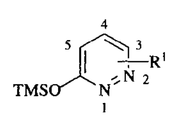
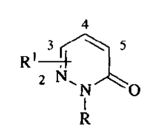
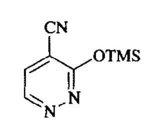
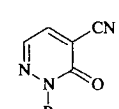
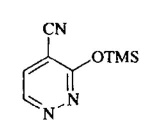
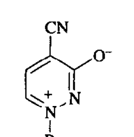
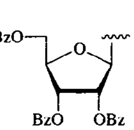
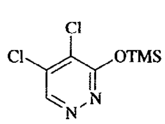
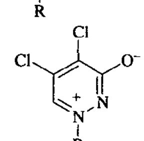
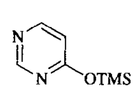
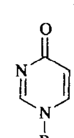
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 1.5 h 2. NH_3, MeOH, rt, 16 h	 (69)	858
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h	 R = 	859
	R^1			
	3-Me		(40)	
	2-Me		(37)	
	3-Et		(55)	
		$SnCl_4$, $Cl(CH_2)_2Cl$		
	X			
	5-F	0°, 30 min; rt, 24 h	(65)	860
	5-F	0°, 15 min; rt, 12 h	(61)	861
	3-F	0°, 30 min; rt, 24 h	(98)	860
	3-Br	rt, 24 h	(56)	861
	5-Me	rt, 18 h	(40)	859
	5-Et	rt, 18 h	(55)	859
	3-F,5-F	0°, 30 min; rt, 24 h	(90)	860
		$SnCl_4$, $Cl(CH_2)_2Cl$		
	R^1			
	3-Cl	45°; rt, 1.5 h	(98)	524
	3-Cl, 4-Cl	reflux, 45 min	(92)	524
	4-Cl, 5-Cl	[$SnCl_4$ only]	(55)	862
	4-Cl, 5-Cl	reflux, 45 min	(88)	863
	3-NO_2, 4-Cl, 5-Cl	reflux, 0.5 h	(62)	524
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 30 min	 (76)	253
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 30 min	 (80) R = 	253
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 30 min	 (55)	253
		$SnCl_4$, $Cl(CH_2)_2Cl$, 15°, 0.5 h; 22°, 3.5 h	 **I** (60) + N^3-isomer (26)	99
		$SnCl_4$, MeCN, 15°, 0.5 h; 22°, 3.5 h	**I** (38) + N^3-isomer (26)	99

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

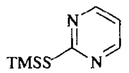
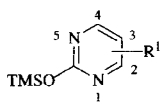
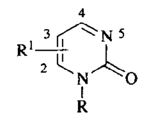
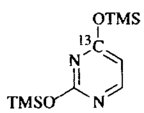
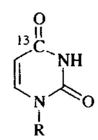
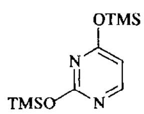
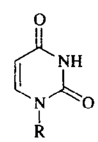
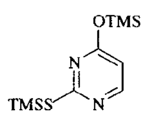
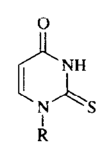
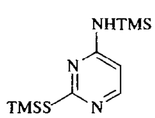
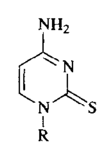
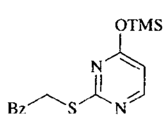
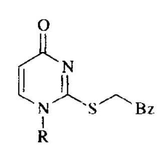
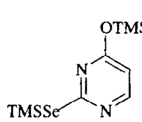
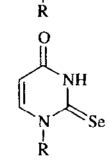
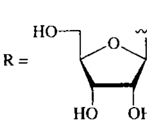
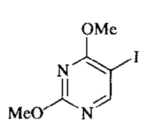
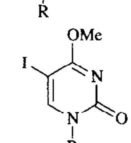
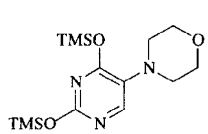
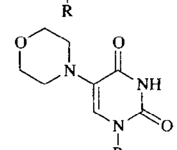
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, 22°, 5 min	 (97)	99
		$SnCl_4$		
	R^1			
	H	MeCN, 22°	(73)	99
	5-F	$Cl(CH_2)_2Cl$, rt, 18 h	(26)	388
	4-Me	MeCN, rt, 12 h	(62)	822
		$SnCl_4$, MeCN, rt, 16 h	 (90)	864
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23°, 12 h	 **I** (84) + N^3-isomer (9)	90
		$SnCl_4$, MeCN, 23°, 12 h	**I** (89) + N^3-isomer (4)	90
		$SnCl_4$, MeCN	 **I** (85)	865
		$SnCl_4$, $Cl(CH_2)_2Cl$, 22°, 2 h	 (95)	84
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 30 min	 (45)	845
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 2. NaOMe, MeOH, rt	 (30) R = 	866
		$SnCl_4$, $Cl(CH_2)_2Cl$, 22°, 2 h	 (67)	84
		$SnCl_4$, MeCN 23°, 1 h	 **I** (53) + N^3-isomer (32) + N^1,N^3-bis(riboside) (12)	90, 193
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23°, 2 h	**I** (39) + N^3-isomer (18) + N^1,N^3-bis(riboside) (42)	90, 193

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

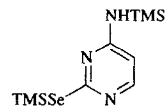
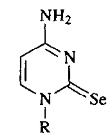
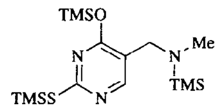
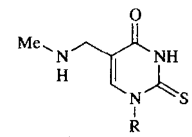
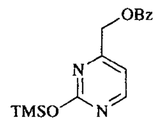
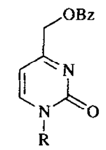
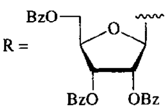
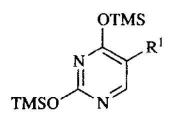
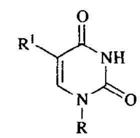
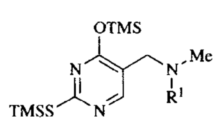
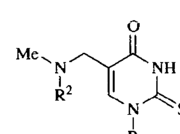
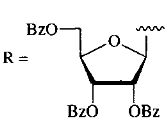
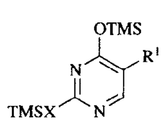
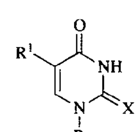
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 3 h 2. NH_3, MeOH, rt	 (31)	811
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 22°, 1 h 2. NH_3, MeOH, 24°, 1 h	 (20)	126
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 2 d	 (18) R = 	867
		$SnCl_4$		
	R^1			
	F	$MeNO_2$, rt, 3 h	(90)	514b
	F	C_6H_6, rt, 3 h	(34)	514b
	F	$Cl(CH_2)_2Cl$, rt, 3 h	(48)	514b
	F	$Cl(CH_2)_2Cl$, rt, 13 h	(99)	868
	F	MeCN, <10°, 1 h	(98)	514b
	F	CH_2Cl_2, rt, 4 h	(86)	869
	Me	—	(—)	870
	Et	$Cl(CH_2)_2Cl$, 22°, 20 h	(95)	84
	Bu-*n*	$Cl(CH_2)_2Cl$, 22°, 5 h	(95)	84
	Bu-*n*	MeCN, 22°, 5 h	(84)	84
	$CH{=}CH_2$	$Cl(CH_2)_2Cl$, rt, 16 h	(58)	808
	$C{\equiv}CH$	$Cl(CH_2)_2Cl$, rt, 4 h	(75)	872
	c-C_3H_5	$Cl(CH_2)_2Cl$, rt, 2 h	(53)	873
	NO_2	$Cl(CH_2)_2Cl$, MeCN, 22°, 0.5 h	(98)	84
	NO_2	$Cl(CH_2)_2Cl$, 23°, 0.1 h	(97)	90, 193
	NO_2	MeCN, 23°, 0.1 h	(98)	90
	OMe	MeCN, rt, 16 h	(62)	874
	OMe	$Cl(CH_2)_2Cl$, 23°, 2.5 h	(53) + N^3-isomer (27) + N^1,N^3-bis(riboside) (13)	90, 193
	OMe	MeCN, 24°, 12 h	(90) + N^3-isomer (3)	193, 90
	OCH_2CF_3	MeCN, 25°, 12 h	(54)	369
	OCH_2CO_2Et	MeCN, rt, 16 h	(67)	874
		$SnCl_4$	 R = 	126
	R^1		R^2	
	Ac	$Cl(CH_2)_2Cl$, 24°, 3 h	(20) + N^3-isomer (19) Ac	126
	$COCF_3$	MeCN	(70-80) $COCF_3$	875
	BOC	$Cl(CH_2)_2Cl$, 24°, 1.5 h	(—) H	126
	$CO_2CH_2CCl_3$	MeCN	(70-80) $CO_2CH_2CCl_3$	875
				
	X R^1			
	O SO_2Me	$SnCl_4$	(—)	876
	S OMe	$SnCl_4$, MeCN	(62) + N^3-anomer (15)	865

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

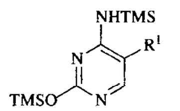
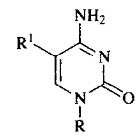
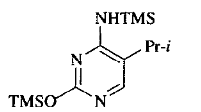
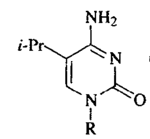
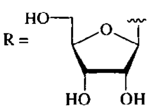
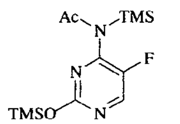
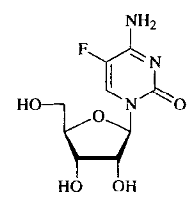
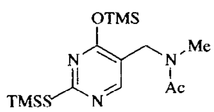
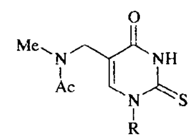
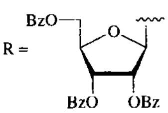
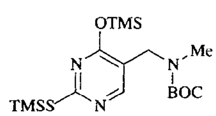
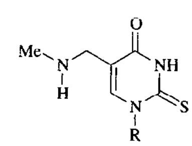
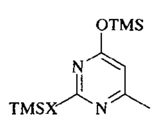
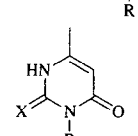
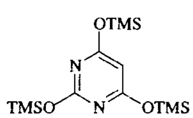
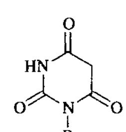
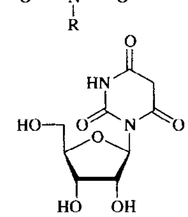
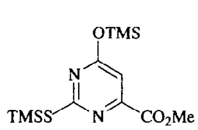
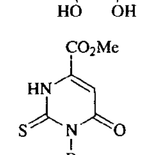
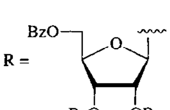
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$,		
	R^1			
	F	MeCN, rt, 3 h	(45)	877
	C≡CH	rt, 2 h	(90)	872
		1. $SnCl_4$ or $SnCl_4/SnBr_4$ 2. NH_3, MeOH	 (72) R = 	878
		1. $SnCl_4$, MeCN, <10°, 15 min; rt, 2 h 2. NaOMe, MeOH	 (67)	514b
		$SnCl_4$, $Cl(CH_2)_2Cl$	 (70) R = 	125, 126
			 (~70)	125, 126
				
	X			
	O	$SnCl_4$, MeCN, 24°	(52) + N^1-isomer (41) + N^1,N^3-bis(riboside) (3)	193,89a
	O	$SnCl_4$, $Cl(CH_2)_2Cl$, 24°	(68) + N^1-isomer (13)	193,89a
	S	$SnCl_4$, MeCN, 22°, 3 h	(39) + *S*-riboside (20)	89a
	S	$SnCl_4$, $Cl(CH_2)_2Cl$, 22°, 4 h	(26)	89a
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (95)	879
		1. $SnCl_4$, MeCN, rt, 6 h 2. NaOMe, MeOH, rt, 3 h	 (70)	544
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 72 h	 (67) R = 	720

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

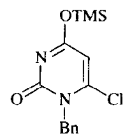
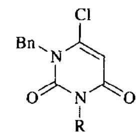
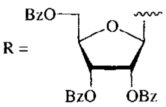
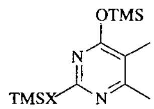
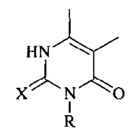
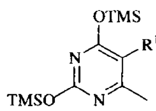
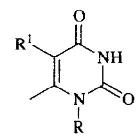
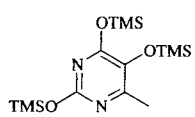
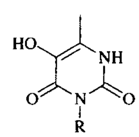
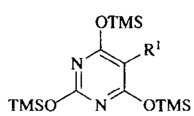
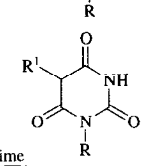
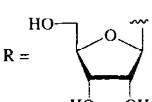
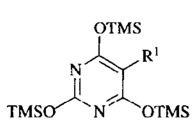
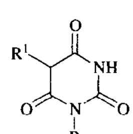
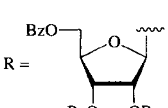
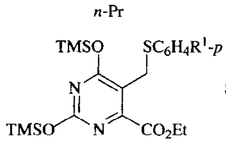
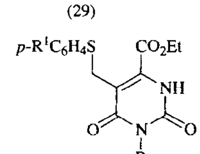
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, 10°, 1 h; rt, 40 h	 (90) R = 	255
		$SnCl_4$		89a
	X			
	O	$Cl(CH_2)_2Cl$, 22°, 6 h	(60) + N^1-isomer (10)	
	O	MeCN, 20°, 2 h	(17) + N^1-isomer (66)	
	S	$Cl(CH_2)_2Cl$, 22°, 5 h	(8)	
	S	MeCN, 20°, 2 h	(20) + *S*-riboside (38)	
		$SnCl_4$		
	R^1			
	Me	MeCN, 22-24°, 12 h	(66) + N^3-isomer (17)	89a, 193
	i-Pr	MeCN, 23°, 24 h	(53) + N^3-isomer (25)	90
	i-Pr	$Cl(CH_2)_2Cl$, rt, 72 h	(18) + N^3-isomer (41)	90
	NO_2	MeCN, 23°, 0.6 h	(73) + bis(riboside) (19)	90
	NO_2	MeCN, 2 h	(73) + N^3-isomer (19)	193
	NO_2	$Cl(CH_2)_2Cl$, 23°, 0.9-1 h	(84) + N^3-isomer (14)	193, 90
		$SnCl_4$	 (40-43)	880
		1. $SnCl_4$ 2. NaOMe, MeOH, rt, time	 R = 	544
	R^1		time	
	Me	MeCN, rt, 24 h	3 h (88)	
	Et	$Cl(CH_2)_2Cl$, rt, 20 h	2 h (93)	
	$CH_2CH{=}CH_2$	MeCN, rt, 20 h	2 h (76)	
	Bn	MeCN, rt, 27 h	2 h (70)	
		$SnCl_4$, MeCN, rt, time	 R = 	364
	R^1	time		
	Me	90 h	(26)	
	n-Pr	40 h	(29)	
		$SnCl_4$, MeCN, 60°, 3 h		809
	R^1			
	F		(17) + N^1,N^3-bis(riboside) (18)	
	Br		(28) + N^1,N^3-bis(riboside) (17)	
	OBu-*n*		(15) + N^1,N^3-bis(riboside) (22)	
	Bu-*t*		(20) + N^1,N^3-bis(riboside) (27)	
	SMe		(22) + N^1,N^3-bis(riboside) (21)	

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

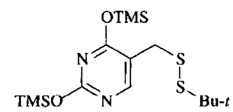
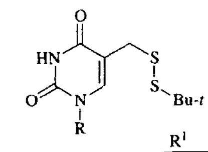
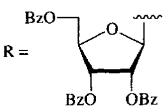
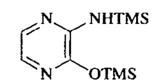
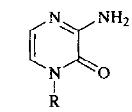
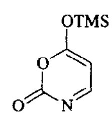
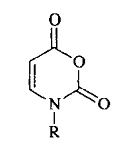
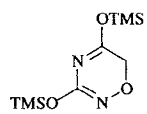
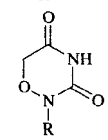
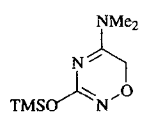
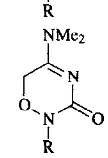
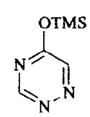
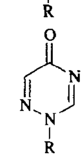
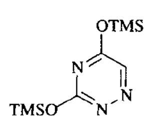
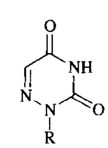
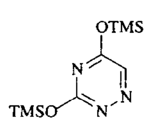
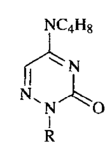
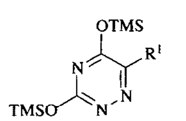
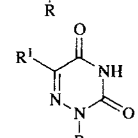
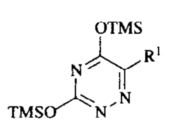
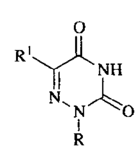
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, rt, 1 h	 (75-93) R = 	881
		$SnCl_4$, $Cl(CH_2)_2Cl$, 25°, 3 h	 R^1: NHTMS (87); H (60); Me (55); $C_{10}H_{21}$ (62)	882; 883; 883; 883
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 2.5 h	 (90)	722
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 22 h	 (68)	726
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h	 (61)	726
		$SnCl_4$, MeCN, 22°, 24 h	 (67)	99
		$SnCl_4$, MeCN, 23°, 12 h	 **I** (93)	90
		$SnCl_4$, $Cl(CH_2)_2Cl$, 23°, 4 h	**I** (97)	90, 84
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 22°, 4 h 2. Pyrrolidine, rt, 3 h	 (57)	79
		$SnCl_4$, $Cl(CH_2)_2Cl$		884
	R^1			
	$NHCH_2CO_2H$		(26) + bis(riboside) (9)	
	$NHCH_2CO_2Me$		(58) + R^1 = $NHCH_2CO_2H$ (5)	
		$SnCl_4$, $Cl(CH_2)_2Cl$		
	R^1			
	Br	rt, 6 h	(87)	885
	c-C_3H_5	rt, 27 h	(30)	873
	N-morpholinyl	rt, 6 h	(71)	885
	3-furyl	rt, 2 h	(88)	546
	SMe	rt, 8 h	(70)	885
	SBn	25°, 12 h	(82)	885

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

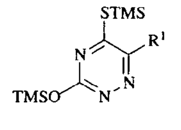
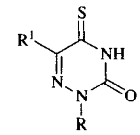
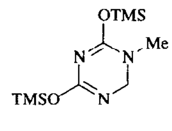
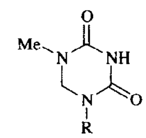
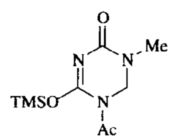
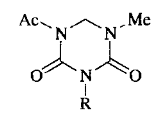
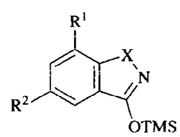
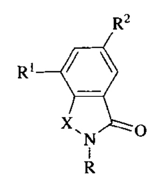
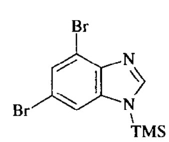
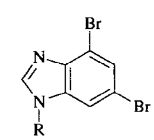
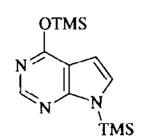
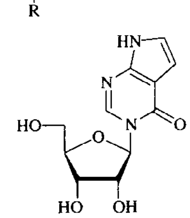
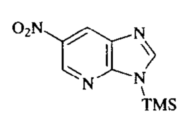
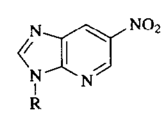
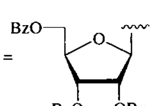
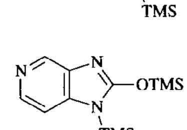
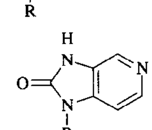
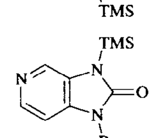
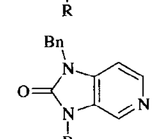
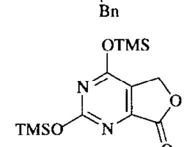
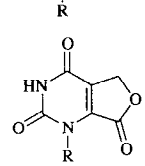
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$		
	R^1			
	SMe	rt, 6 h	(80)	886
	SBn	rt, 8 h	(84)	886
		$SnCl_4$, C_6H_6, 25°, 18 h	 (18)	239
		$SnCl_4$, MeCN, rt, 94 h	 (41)	239
		$SnCl_4$, $Cl(CH_2)_2Cl$ reflux, 40 min; rt, 30 min		887
	R^1 R^2 X			
	H H O		(74)	
	Me H O		(63)	
	H Me S		(69)	
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 (25) + N^3-isomer (11)	849
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. NH_3, MeOH, rt, 24 h	 (25)	888
		$SnCl_4$, MeCN, rt, 12 h	 (35) + α-anomer (11) R = 	889
		$SnCl_4$, $Cl(CH_2)_2Cl$/MeCN (1:1), 0°, 7 h	 (23) + N^3-isomer (19)	890
		$SnCl_4$, $Cl(CH_2)_2Cl$/MeCN (1:1), 0°, 7 h	 (31)	890
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 5 h	 **I** (18) + bis(riboside) (81)	891
		$SnCl_4$, MeCN, 0-5°, 0.5 h	**I** (81)	891

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

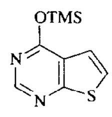
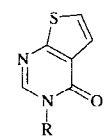
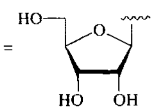
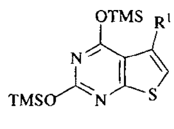
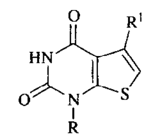
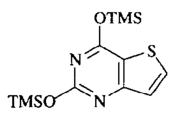
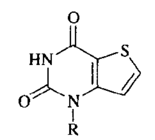
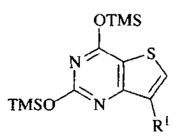
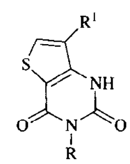
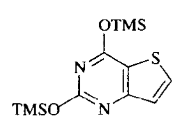
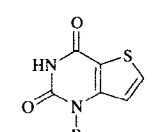
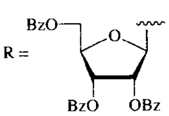
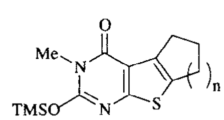
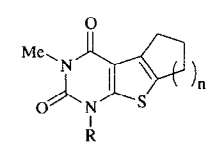
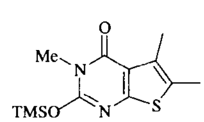
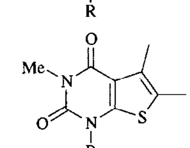
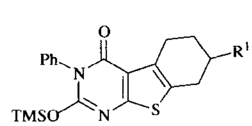
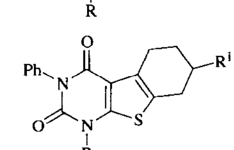
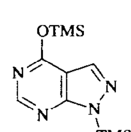
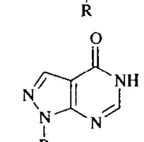
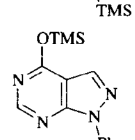
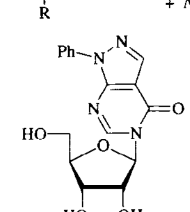
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. NH_3, MeOH, rt, 24 h	 (25) R = 	888
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18-20 h 2. NH_3, MeOH, rt, 20 h	 R^1: H (30); Me (51)	525
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. NH_3, MeOH, rt, 3 d	 (67)	892
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, -30°, 8 h 2. NH_3, MeOH		659
	R^1		/ N^1-isomer	
	FC_6H_4		(34) / (24)	
	ClC_6H_4		(23) / (18)	
	BrC_6H_4		(24) / (20)	
	Me		(41) / (—)	
	Ph		(36) / (—)	
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h	 (98) R = 	893
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 n: 1 (70); 2 (23)	894
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (26)	894
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 R^1: H (41); Me (45)	894
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60°, 6 h	 **I** (17) + N^2-isomer (7) + N^5-isomer (12) + N^1,N^5-bis(riboside) (38) + N^2,N^5-bis(riboside) (9)	735, 510
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. NH_3, MeOH, rt, 24 h	 (30)	888

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

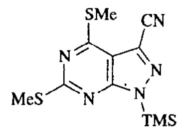
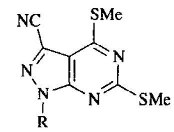
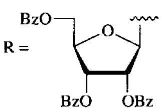
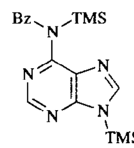
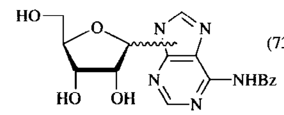
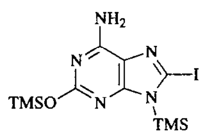
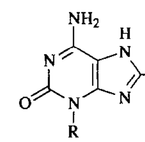
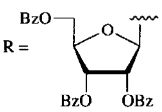
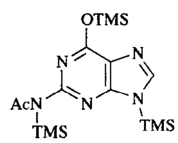
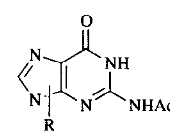
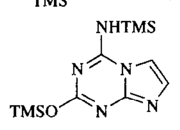
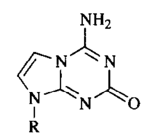
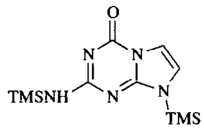
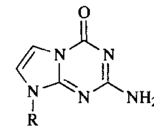
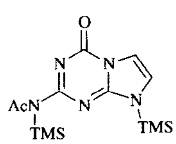
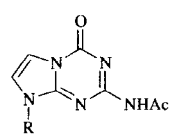
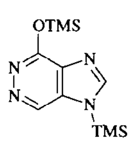
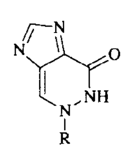
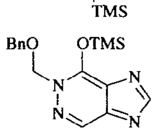
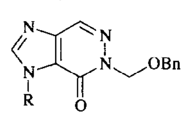
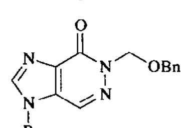
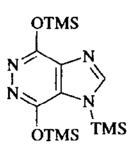
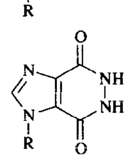
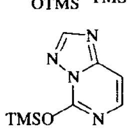
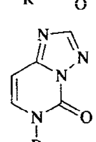
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 2 h	 (96) R = 	895
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, 48-72 h 2. NH_3, MeOH	 (73) N^7:N^9 = 1:1	101
		$SnCl_4$, $Cl(CH_2)_2Cl$ rt, 18 h	 (—) R = 	896
		$SnCl_4$, MeCN, rt, 4 h	 (81) N^7:N^9 = 3:1	142
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 4 h	 (60)	897
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 30 h	 (56)	898
		$SnCl_4$, MeCN, rt, 30 h	 (85)	898
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 15 min	 sugar:base / (yield) / N^3,N^6-bis(riboside) 1:1 (74) (20) 1.5:1 (40) (40) 2:1 (50) (44)	543
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 1 h	 **I** (56) + N^3-isomer **II** (13)	899
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 3 d	 **II** (33) + N^1-isomer **I** (18)	900
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (38) + N^1,N^5 and N^1,N^6 bis(ribosides) (58)	543
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 24 h	 (31)	743

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

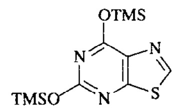
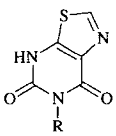
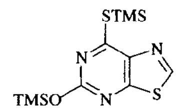
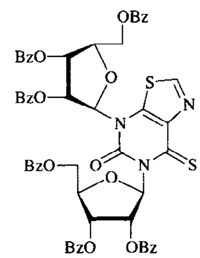
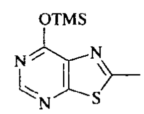
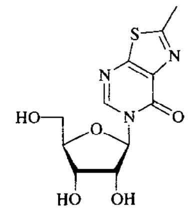
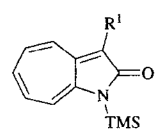
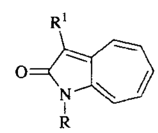
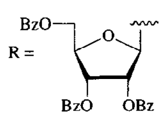
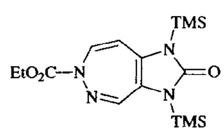
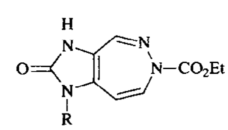
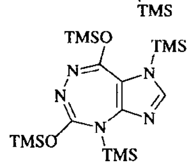
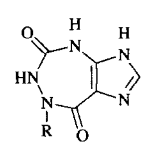
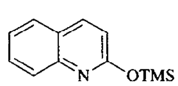
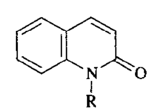
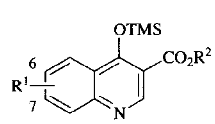
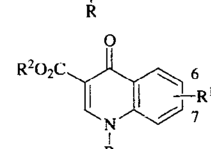
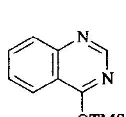
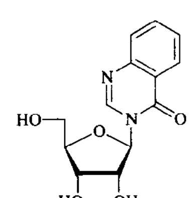
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 4 h	 (56)	901
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 15 h	 (—)	901
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. NH_3, MeOH, rt, 24 h	 (25)	888
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 1 h	 R^1: H (56); CO_2Me (69); R = 	902
		$SnCl_4$, $Cl(CH_2)_2Cl$, MeCN, 0°, 7 h	 (20) + N^3-isomer (15) + N^1,N^3-bis(riboside) (13)	890
		$SnCl_4$, CH_2Cl_2, MeCN	 (39) + N^3-isomer (2)	507
		$SnCl_4$, MeCN, 22°, 42 h	 (79)	99
		$SnCl_4$, $Cl(CH_2)_2Cl$		
	R^1 / R^2			
	H / Et	22°, 2 h	(82)	99
	7-Me / Et	rt, 3 h	(82)	740
	6-F / Et	rt, 3 h	(83)	740
	6,7-F_2 / Et	rt, 3 h	(94)	740
	6-F,7-Cl / H	rt, 3 h	(18)	740
	6-F,7-Cl / Et	rt, 3 h	(60)	740
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, rt, 18 h 2. NH_3, MeOH, rt, 24 h	 (27)	888

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

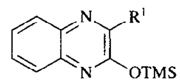
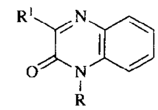
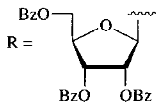
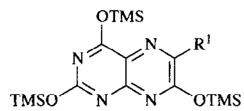
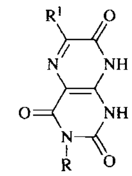
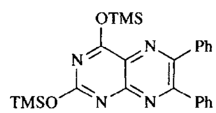
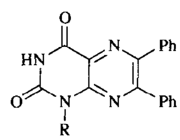
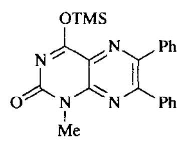
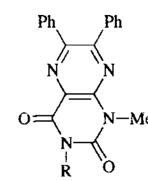
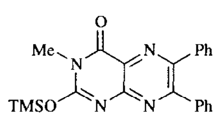
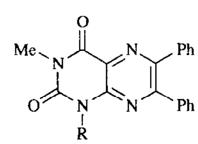
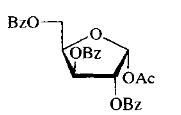
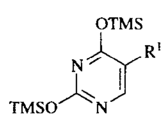
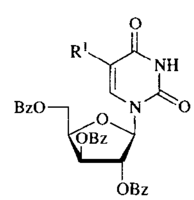
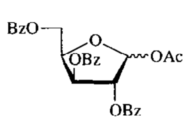
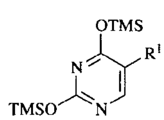
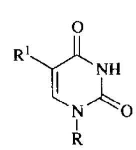
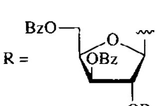
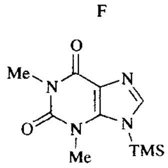
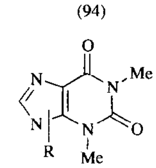
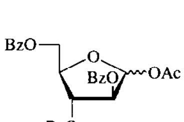
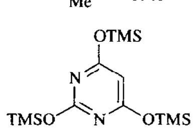
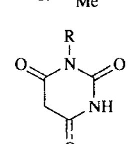
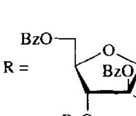
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN	 R = 	903
	R^1			
	H	rt, 3 d	(8)	
	Me	50°, 20 h	(5)	
		$SnCl_4$, C_6H_6, reflux, 4 h	 R^1: H (19); Me (23); Ph (52)	904; 904; 904
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 4 h	 (20) + N^3-isomer (8) + bis(riboside) (21)	905
		$SnCl_4$, CH_2Cl_2, rt, 1 d	 (48)	906
		$SnCl_4$, CH_2Cl_2, rt, 1 d	 (32)	906
		$SnCl_4$, $Cl(CH_2)_2Cl$, 22°, 8 h	 R^1: H (90); F (90); Me (91)	907
		$SnCl_4$, 2 h	R^1 = F, (80)	908
		$SnCl_4$, MeCN, time	 R = 	
	R^1	time		
	H	3-5 h	(80)	907
	F	12 h	(94)	908
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 30 min	 (—) N^7:N^9 = 4:1	738
		$SnCl_4$, MeCN, rt, 12 h	 (50) R = 	364

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

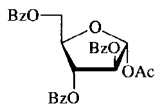
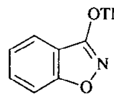
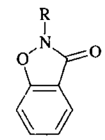
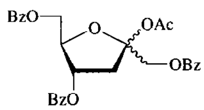
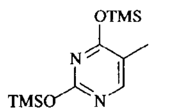
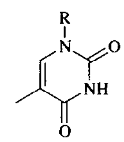
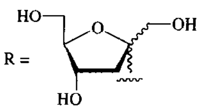
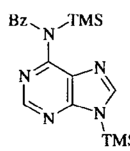
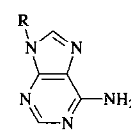
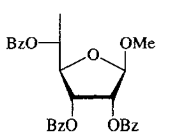
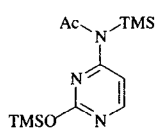
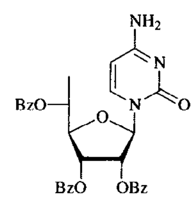
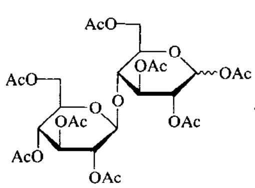
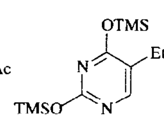
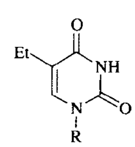
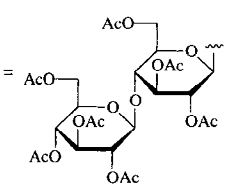
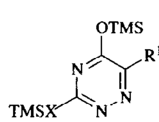
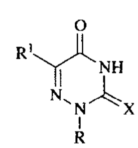
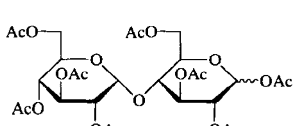
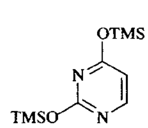
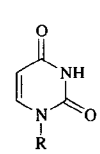
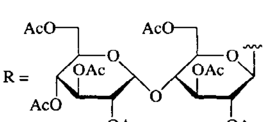
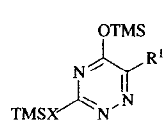
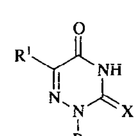
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 40 min; rt, 30 min	 (74)	887
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, −20° to rt, 1 h 2. NH_3, MeOH	 **I** (58) α:β = 1:5 R = 	693
		1. $SnCl_4$, MeCN, −20° to rt, 1 h 2. NH_3, MeOH	**I** (62) α:β = 1:3	693
		1. $SnCl_4$, $Cl(CH_2)_2Cl$, −20° to rt, 1 h 2. NH_3, MeOH	 **I** (64) α:β = 30:1	693
		1. $SnCl_4$, MeCN, −20° to rt, 1 h 2. NH_3, MeOH	**I** (61) α:β = 11:1	693
		$SnCl_4$, $Cl(CH_2)_2Cl$, 80°, 2 h	 (83)	911
		$SnCl_4$, $Cl(CH_2)_2Cl$, 80°, 2 h	 (78) R = 	98
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 2 h		98
	X R^1			
	O H		(80)	
	O Me		(63)	
	S Me		(95)	
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 2 h	 (71) R = 	98
		$SnCl_4$, $Cl(CH_2)_2Cl$		98
	X R^1			
	O H	reflux, 2 h	(72)	
	O Me	60°, 4 h	(63)	
	S Me	60°, 4 h	(70)	

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

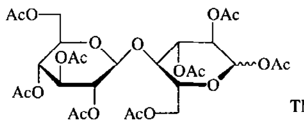
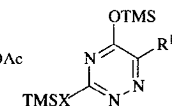
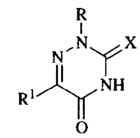
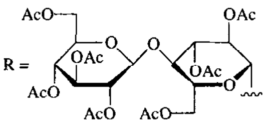
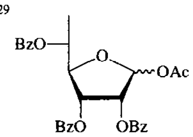
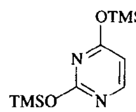
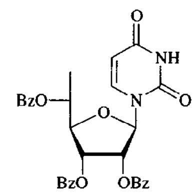
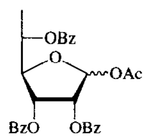
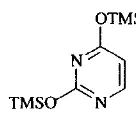
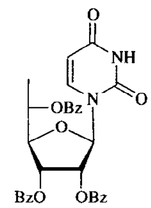
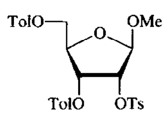
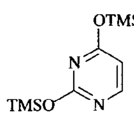
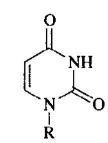
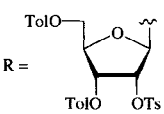
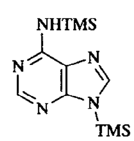
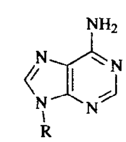
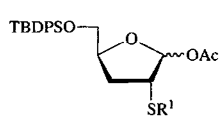
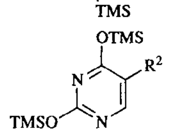
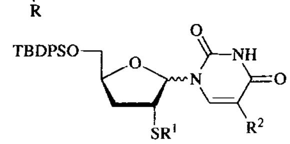
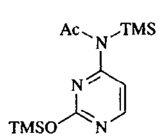
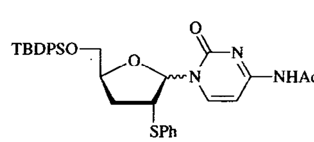
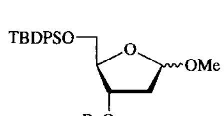
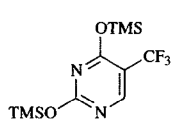
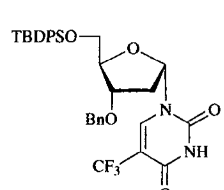
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 2 h	 R = 	98
	X R[1]			
	O H		(80)	
	O Me		(69)	
C29	S Me		(66)	
		$SnCl_4$, MeCN	 (—)	912
		$SnCl_4$, MeCN	 (—)	912
		$SnCl_4$	 (—) R = 	192k
		$SnCl_4$	 (—)	192k
		$SnCl_4$		
R[1]	R[2]			
$C_6H_4NO_2$-*o*	Me	CH_2Cl_2, –78 to 25°, 5 h	(—) α:β = 1:9	227
Ph	H	$Cl(CH_2)_2Cl$, rt, 12 h	(96) α:β = 3:97	229
Ph	H	$Cl(CH_2)_2Cl$, 0°, 12 h	(91) α:β = 7:93	229
Ph	H	$Cl(CH_2)_2Cl$ (6 eq), rt	(96) α:β = 3:97	228
Ph	H	$Cl(CH_2)_2Cl$ (1.8 eq), 0°, 3.5 h	(91) α:β = 7:93	228
Ph	Me	$Cl(CH_2)_2Cl$, 0°, 12 h	(87) α:β = 8:92	229
Ph	Me	$Cl(CH_2)_2Cl$, 0°, 4 h	(87) α:β = 8:92	228
Ph	Me	CH_2Cl_2, –78 to 25°	(—) α:β = 1:14	227
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0°, 4-12 h	 I (93) α:β = 11:89	228, 229
		$SnCl_4$, CH_2Cl_2, 5°, 1.5 h	 (5) + β-anomer (4)	913

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

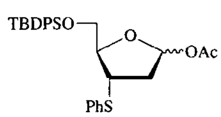
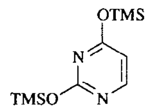
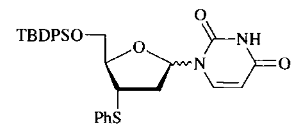
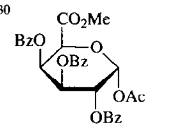
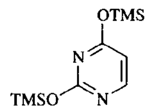
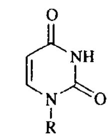
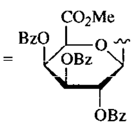
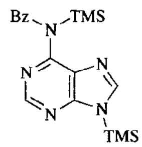
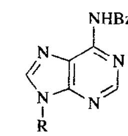
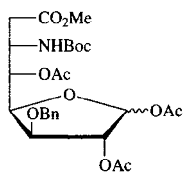
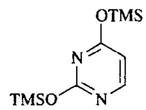
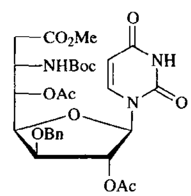
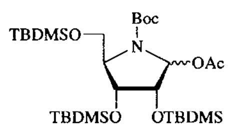
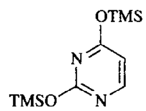
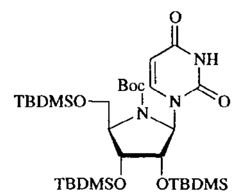
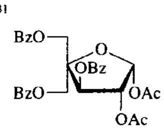
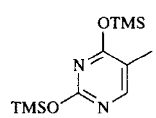
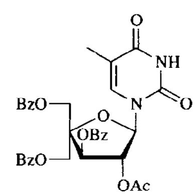
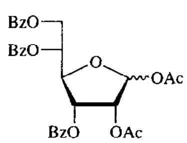
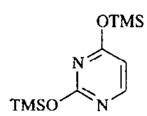
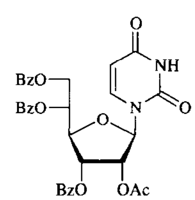
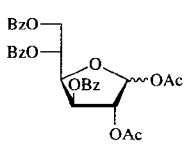
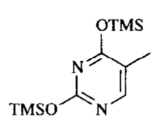
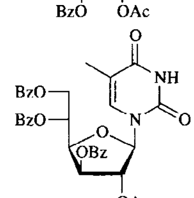
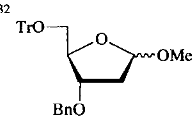
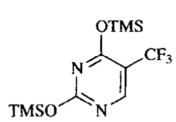
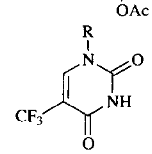
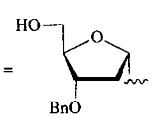
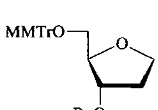
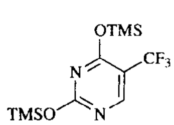
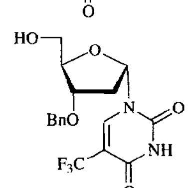
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, CH_2Cl_2, rt, 12 h	 (70) α:β = 53:47	229
C_{30} 		$SnCl_4$, $Cl(CH_2)_2Cl$, 70°, 5 h	 (75) R = 	766
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 5 h	 (65)	100
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 28 h	 (85)	785
		$SnCl_4$, $Cl(CH_2)_2Cl$, 0 to 20°	 (73) α:β = 8:92	783
C_{31} 		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (71)	914
		$SnCl_4$, MeCN, rt, 24 h	 (63)	833
		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (66)	915
C_{32} 		$SnCl_4$, CH_2Cl_2, MeCN, <5°, 30 min	 (31) + β-anomer (22) R = 	913
		$SnCl_4$, MeCN, −5°, 20 min	 (33) + β-anomer (13)	913

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

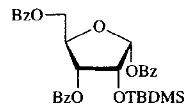
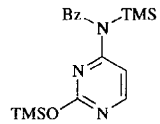
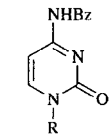
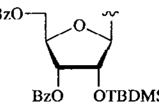
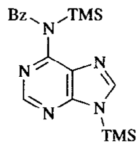
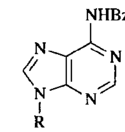
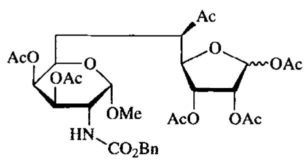
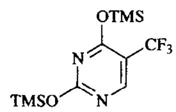
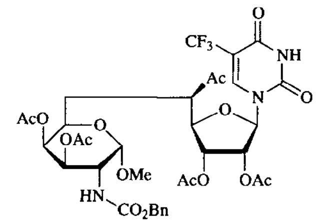
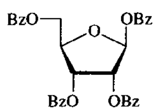
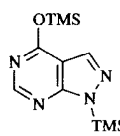
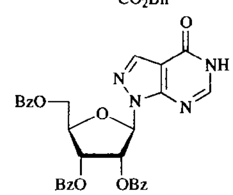
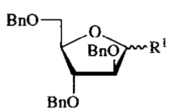
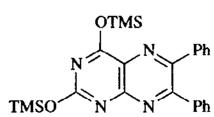
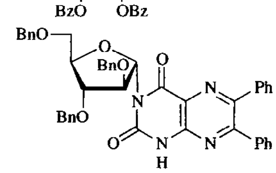
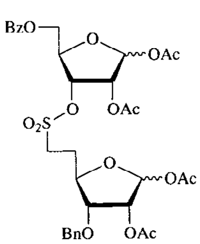
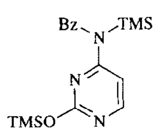
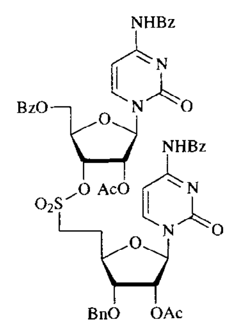
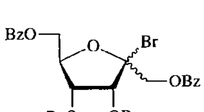
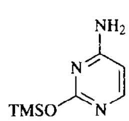
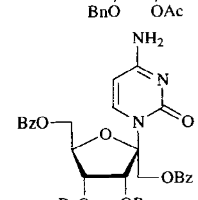
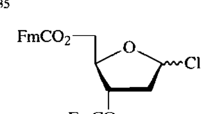
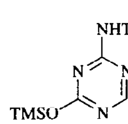
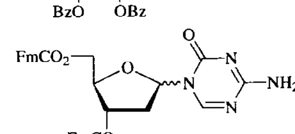
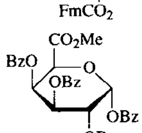
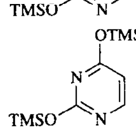
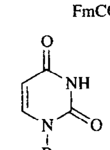
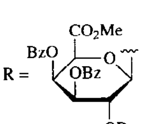
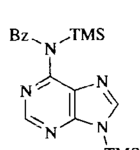
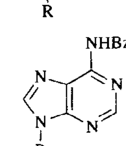
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux	 (95) R = 	846
		$SnCl_4$, $Cl(CH_2)_2Cl$, reflux	 (93)	846
		$SnCl_4$, $Cl(CH_2)_2Cl$	 (75)	916
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 5 h	 (39)	100
 $R^1 = O_2CC_6H_4NO_2$-*p*		$SnCl_4$, CH_2Cl_2, rt, 5 d	 (33)	917
		$SnCl_4$	 (76)	508
C_{34} 		$SnCl_4$, $Hg(CN)_2$, C_6H_6, 60°, 1.5 h	 (56)	632, 918
C_{35} 		$SnCl_4$, $Cl(CH_2)_2Cl$, rt, 2 h	 (45) α:β = 1:0.9	919
		$SnCl_4$, $Cl(CH_2)_2Cl$, 70°, 5 h	 (75) R = 	766
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60-70°, 5 h	 (65)	100

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST *(Continued)*

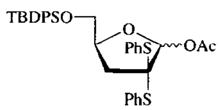
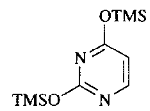
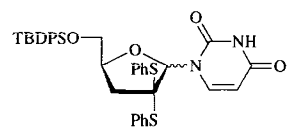
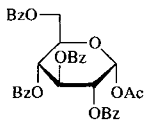
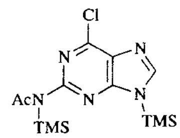
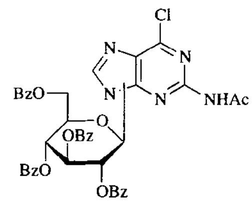
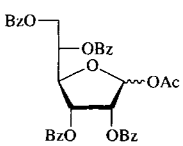
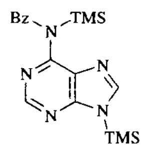
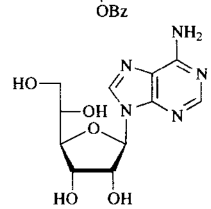
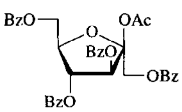
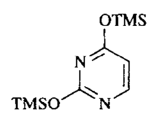
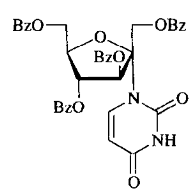
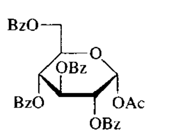
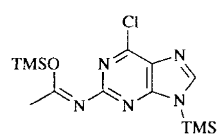
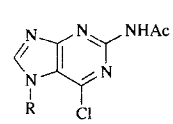
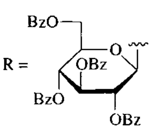
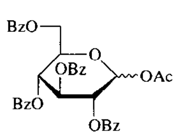
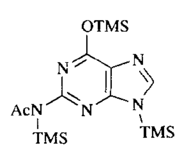
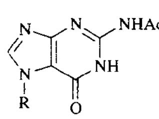
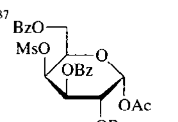
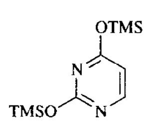
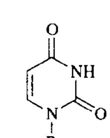
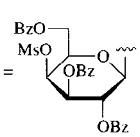
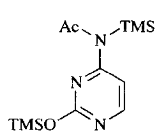
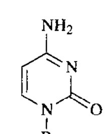
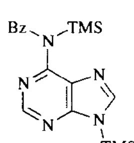
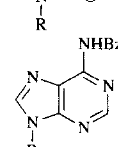
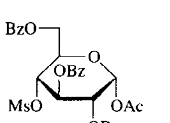
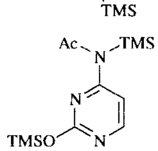
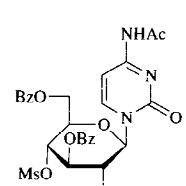
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, 30 min	 (64) α:β = 23:77	305a
		$SnCl_4$, MeCN, rt, 24 h	 (65) N^9:N^7 = 10:90	409
C_{36} 		1. $SnCl_4$, $Cl(CH_2)_2Cl$, reflux, 2 h 2. NaOMe, MeOH, reflux, 1 h	 (68)	780
		$SnCl_4$, MeCN, rt, 1 h	 (88)	920
		$SnCl_4$, MeCN, rt, 1 h	 (59) + N^9-isomer (7) R = 	409
		$SnCl_4$, MeCN, rt, 4 h	 (61)	142
C_{37} 		$SnCl_4$, $Cl(CH_2)_2Cl$, 60°, 12 h	 (71) R = 	766
		$SnCl_4$, $Cl(CH_2)_2Cl$, 60°, 12 h	 (85)	766
		$SnCl_4$, $Cl(CH_2)_2Cl$, MS, 60-70°, 5 h	 (59)	100
		$SnCl_4$, CH_2Cl_2, 60°, 12 h	 (81)	921

TABLE III. REACTIONS OF SILYLATED HETEROCYCLIC BASES WITH PROTECTED SUGARS - $SnCl_4$ CATALYST (*Continued*)

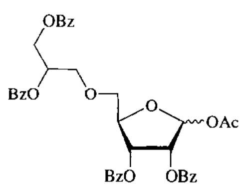
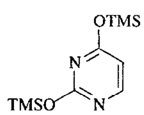
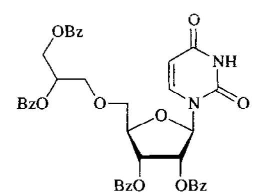
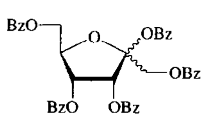
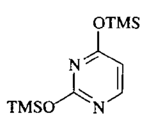
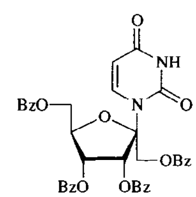
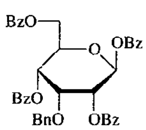
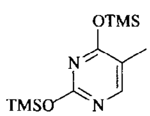
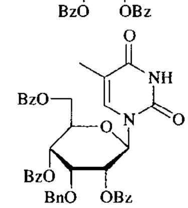
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$, MeCN, rt, 2 d	 (72)	871
		$SnCl_4$, MeCN	 (81)	918
		$SnCl_4$, $Cl(CH_2)_2Cl$, 40°, 4 h	 (80)	922

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES

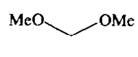
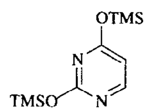
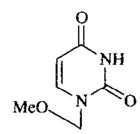
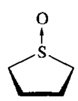
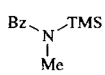
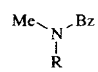
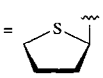
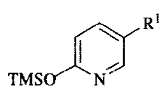
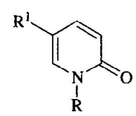
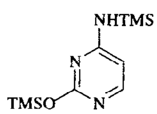
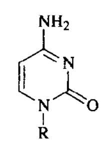
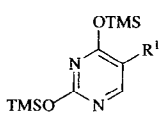
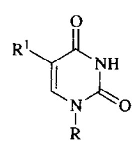
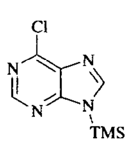
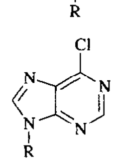
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		TMSOTf, CH_2Cl_2, −30°, 2-12 h	 (74)	923
C_4 		TMSOTf, Et_3N, ZnI_2, PhMe, rt, 48 h	 (63) R = 	414
		TMSOTf, Et_3N, ZnI_2, PhMe, rt, 48 h	 R^1: H (47); Cl (65)	414
		TMSOTf, Et_3N, ZnI_2, PhMe, rt, 48 h	 (61)	414
		TMSOTf, Et_3N, ZnI_2, PhMe, rt, 48 h	 R^1: H (67); F (53); Me (84)	414
		TMSOTf, Et_3N, ZnI_2, PhMe, rt, 48 h	 (59)	414

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

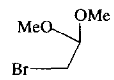
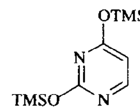
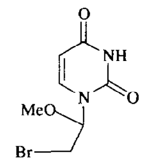
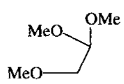
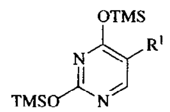
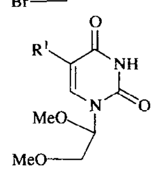
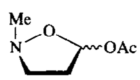
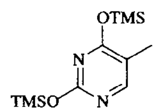
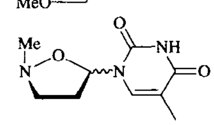
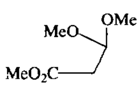
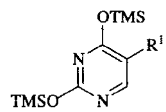
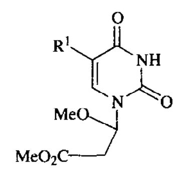
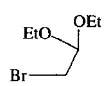
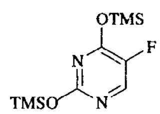
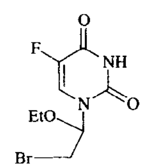
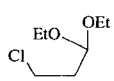
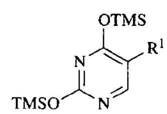
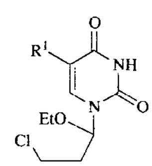
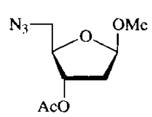
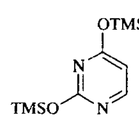
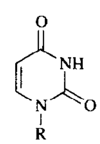
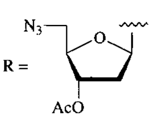
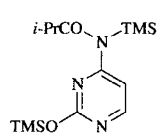
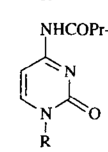
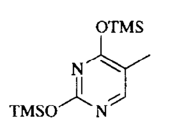
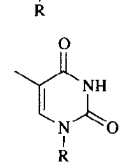
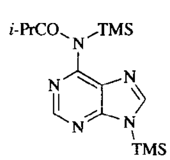
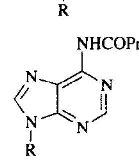
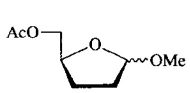
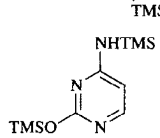
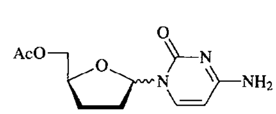
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 (40)	923
C_5 		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 R^1: H (81); F (83)	923
C_6 		TMSOTf,CH_2Cl_2, 25°, 3 h	 (70)	924
		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 R^1: H (56); F (81)	923
		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 (71)	923
C_7 		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 R^1: H (56); F (91)	923
C_8 		TMSOTf, MeCN, –40 to 0°, 6 h; rt, 16 h	 (35) + α-anomer (13) R = 	925
		TMSOTf, MeCN, –40 to 0°, 4 h; rt, 24 h	 (24) + α-anomer (10)	925
		TMSOTf, MeCN, –40 to 0°, 8.5 h rt, 16 h	 (18) + α-anomer (7)	925
		TMSOTf, MeCN, –40 to 0°, 4 h	 (5) + α-anomer (2)	925
		TBDMSOTf, MeCN, 25°, 12 h	 (80) α:β = 1.4:1	926

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

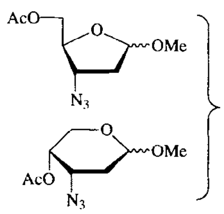
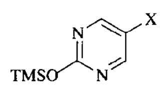
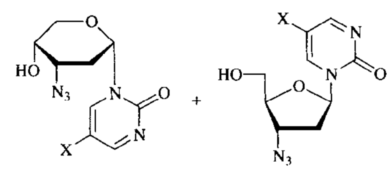
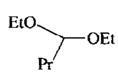
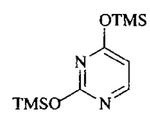
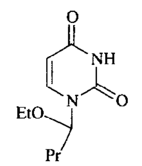
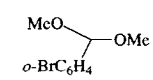
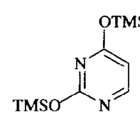
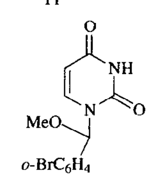
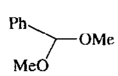
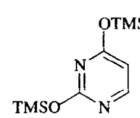
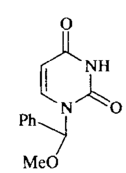
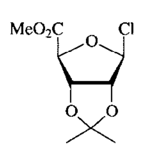
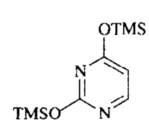
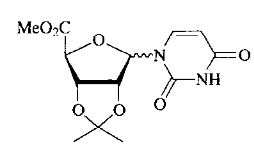
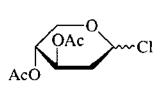
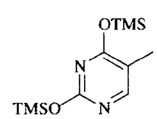
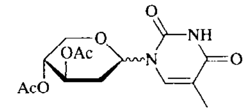
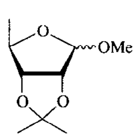
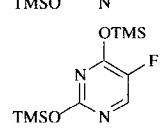
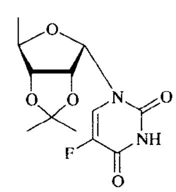
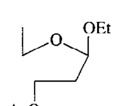
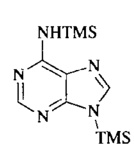
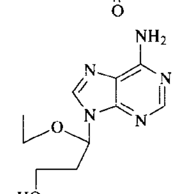
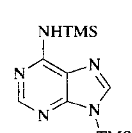
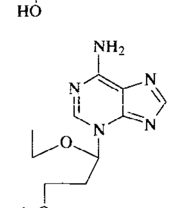
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
	 X: Br, I	1. TMSOTf 2. NH_3, MeOH	 Br: (17) + (12); I: (15) + (15)	149
		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 (77)	923
C_9				
		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 (74)	923
		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 (91)	923
		$AgClO_4$, C_6H_6, 25°, 15 h	 (60) α:β = 3:1	224
		$AgClO_4$, C_6H_6, rt, 15 min	 (80)	927
		TMSOTf, CH_2Cl_2, rt, 15-20 h	 (44)	220
		1. TMSOTf, MeCN, 30°, 2 d 2. NH_3, MeOH	 (50)	555
		TMSOTf, MeCN, 30°, 4 h	 (60-75)	666

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

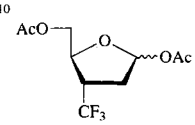
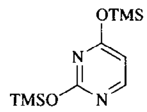
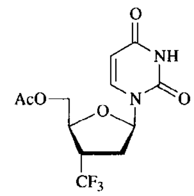
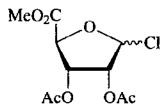
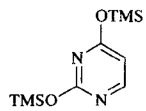
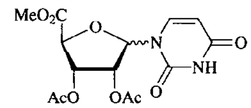
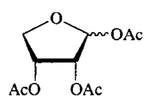
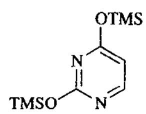
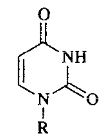
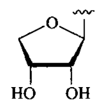
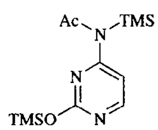
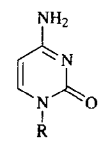
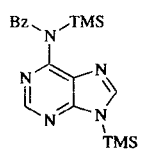
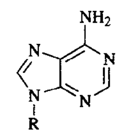
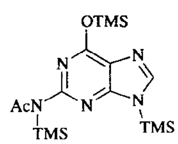
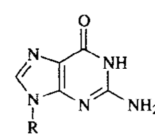
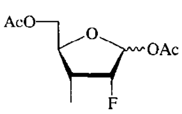
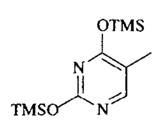
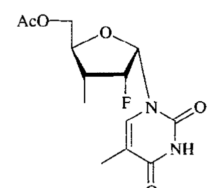
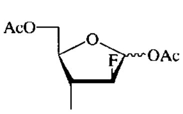
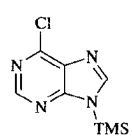
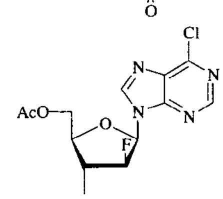
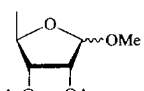
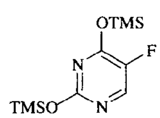
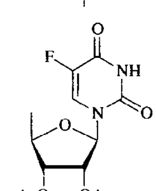
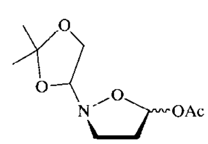
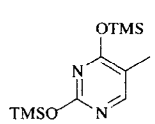
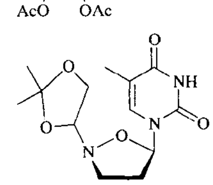
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 40 min	 (—)	296
		$AgClO_4$, C_6H_6, 25°, 18 h	 (34) α:β = 1:4	224
		1. TMSOTf, MeCN, reflux, 2 h 2. NH_3, MeOH, 25°, 24 h	 (43) R = 	928
		1. TMSOTf, MeCN, reflux, 2 h 2. NH_3, MeOH, 25°, 24 h	 (55)	928
		1. TMSOTf, MeCN, reflux, 5 h 2. NH_3, MeOH, 25°, 24 h	 (63)	928
		1. TMSOTf, MeCN, reflux, 3 h 2. NH_3, MeOH, 25°, 24 h	 (25)	928
		TMSOTf, MeCN, rt, 12 h	 (55) + β-anomer (28)	392
		TMSOTf, MeCN, 0°, 2 d	 (31) + N^9-α-isomer (17) + N^7-α-isomer (17) + N^7-β-isomer (11)	392
		TMSOTf, CH_2Cl_2, rt, 20 h	 (58)	221
		TMSOTf, CH_2Cl_2, 25°, 3 h	 (44)	924

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

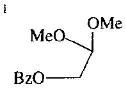
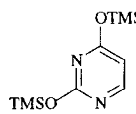
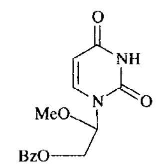
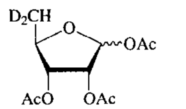
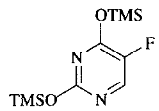
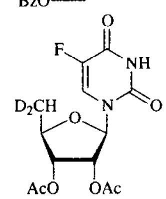
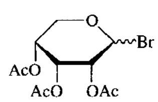
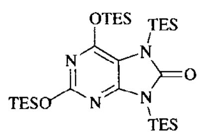
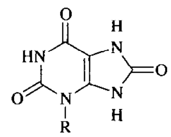
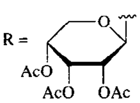
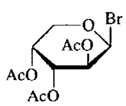
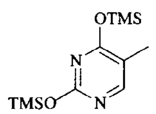
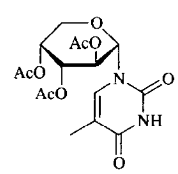
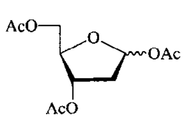
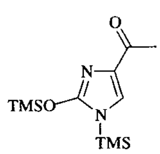
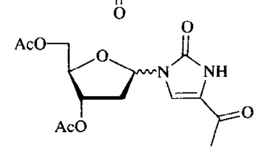
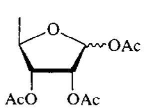
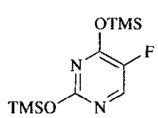
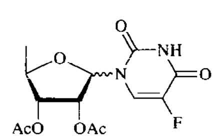
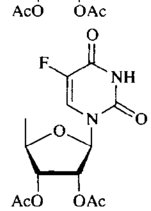
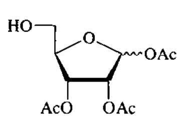
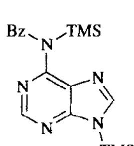
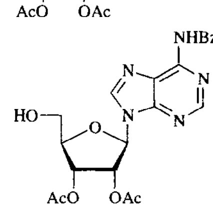
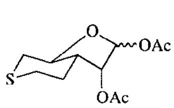
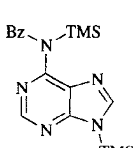
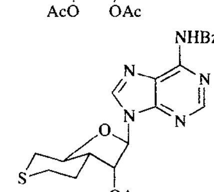
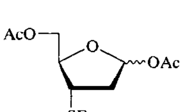
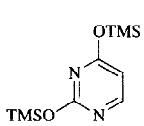
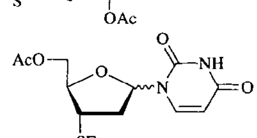
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 (66)	923
		TMSOTf, CH_2Cl_2, rt, 5 h	 (58)	221
		$AgClO_4$, PhMe, 60°	 (56) R = 	74
		$AgClO_4$, C_6H_6, rt, 16 h	 (78)	80
		TMSOTf, $Cl(CH_2)_2Cl$, –40° to rt, 0.5 h	 (49)	929
		TMSOTf	 (—) α:β = 1:9	220
		TMSOTf, CH_2Cl_2, rt, 20 h	 (65) + α-anomer (6)	221, 930
		TMSOTf, $Cl(CH_2)_2Cl$, 20°, 16 h	 (55)	931
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 15 h	 (88)	932
		TMSOTf, MeCN, –30°, 2 h	 (57)	933

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

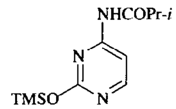
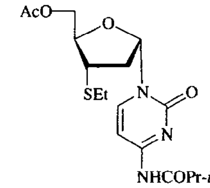
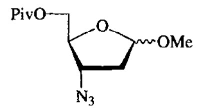
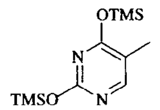
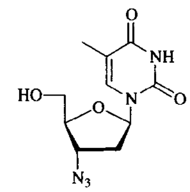
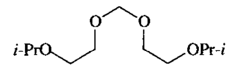
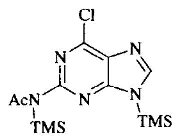
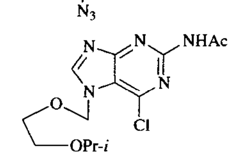
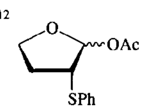
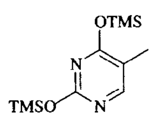
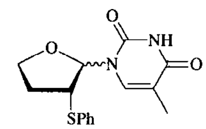
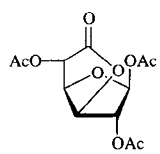
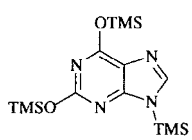
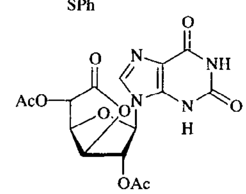
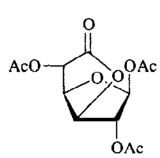
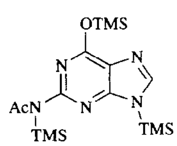
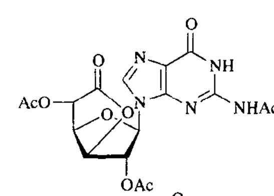
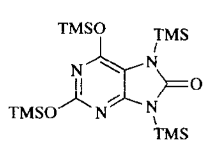
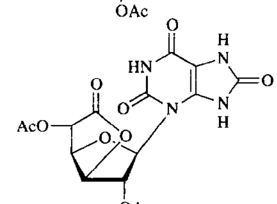
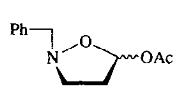
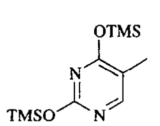
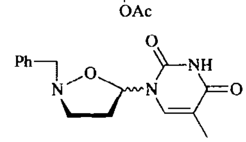
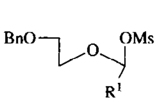
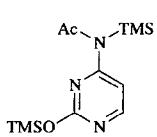
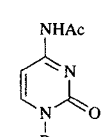
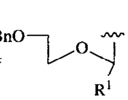
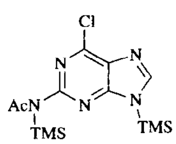
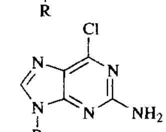
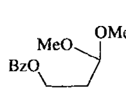
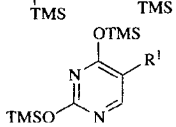
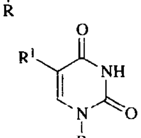
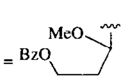
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, MeCN, −30°, 2 h	 (21) + β-anomer (13)	933
		1. TMSOTf, MeCN, 0°, 30 min 2. NaOMe, MeOH, rt, 1 h	 (33)	934
		TMSOTf, $Cl(CH_2)_2Cl$, −30°, 2 h	 (58) N^7:N^9 = 10:1	521
C_{12} 		TMSOTf, CH_2Cl_2, 25°	 (—) α:β = 1:4	227
		TMSOTf, $Cl(CH_2)_2Cl$, 70°, 16 h	 (42) + N^7-isomer (22)	935
		TMSOTf, $Cl(CH_2)_2Cl$, 70°, 16 h	 (49) + N^7-isomer (35)	935
		TMSOTf, $Cl(CH_2)_2Cl$, 60°, 15 h	 (54)	935
		TMSOTf, CH_2Cl_2, 25°, 3 h	 (75)	924
		TMSOTf, CH_2Cl_2	 R^1: CF_3 (29); CF_2H (42); R = 	936
		TMSOTf, CH_2Cl_2	 R^1: CF_3 (8); CF_2H (31); N^7:N^9 = 1:1	936
		TMSOTf, CH_2Cl_2, −30°, 2-12 h	 R^1: H (80); F (71); R = 	923

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

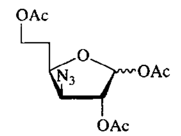
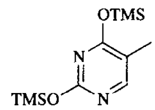
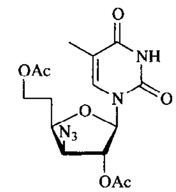
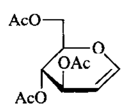
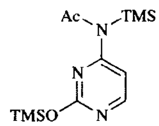
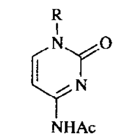
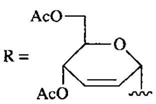
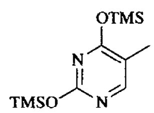
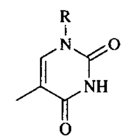
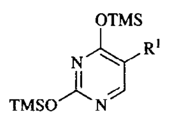
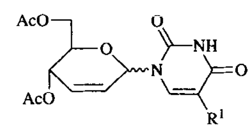
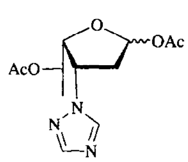
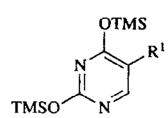
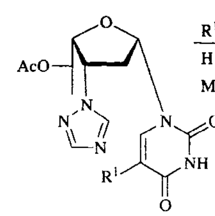
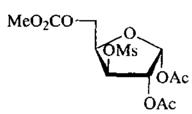
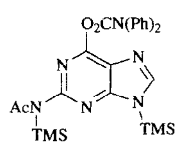
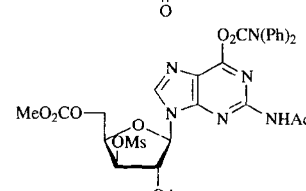
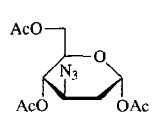
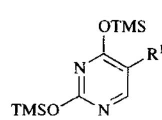
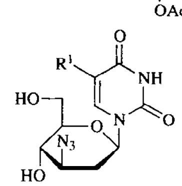
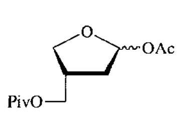
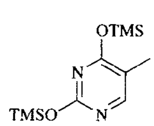
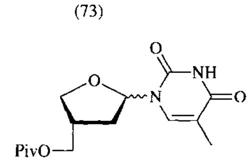
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, MeCN, rt	 (41)	937
		TMSOTf, CH_2Cl_2, rt, 30 min	 (46) + β-anomer (25) R = 	306
		TMSOTf, CH_2Cl_2, rt, 55 min	 (21) + β-anomer (25)	306
		TMSOTf, MeCN, 0°		310
	R¹		α:β	
	N(Me)Bn		(67) 1:1	
	1-pyrrolidinyl		(74) 1:1	
	NHC_6H_4OEt-*p*		(39) 1:1	
	N-4-methylpiperidinyl		(62) 1:1	
	N-4-methylpiperazinyl		(39) 1:1	
	N-4-benzylpiperazinyl		(63) 1:1	
		TMSOTf, MeCN, 0°, 2 h	 R¹ / β-anomer: H (32) (18); Me (32) (13)	531
		TMSOTf, PhMe, 80°, 2 h	 (49)	938
		1. TMSOTf, $Cl(CH_2)_2Cl$, rt, 5 h 2. NH_3, MeOH		939
	R¹			
	H		(56)	
	F		(66)	
	Cl		(73)	
	Br		(84)	
	I		(86)	
	Me		(73)	
		TMSOTf, MeCN, −5 to 0°, 2 h	 (37) α:β = 1:3	139a

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

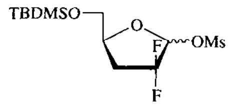
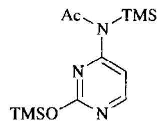
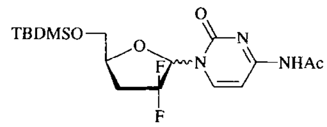
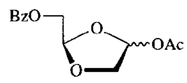
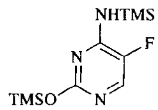
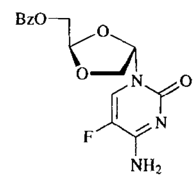
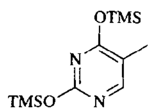
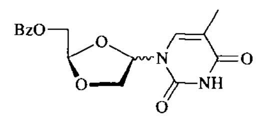
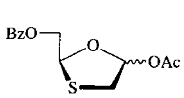
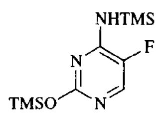
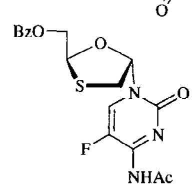
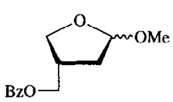
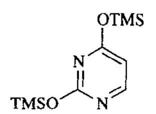
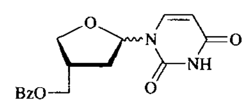
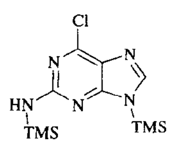
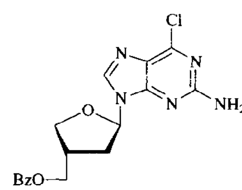
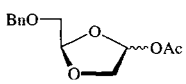
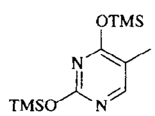
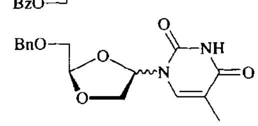
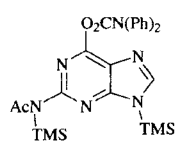
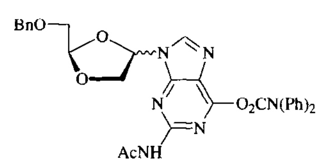
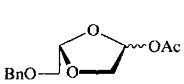
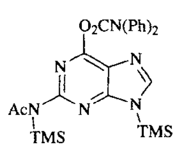
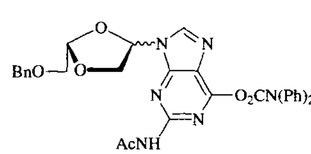
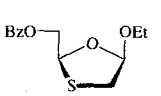
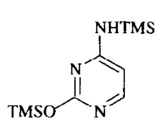
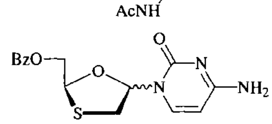
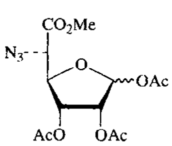
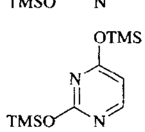
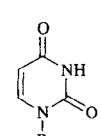
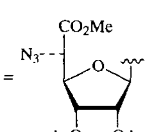
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 4 h	 (44) α:β = 1:1	506
C_{13} 		1. TMSOTf, CH_2Cl_2, 0°, 20 min 2. rt, 2 h 3. Ac_2O, DMAP	 (46) + β–anomer (30)	940
		TMSOTf, MeCN, 25°, 66 h	 (76) α:β = 1:1	942
		1. TMSOTf, CH_2Cl_2, MS, 0°, 20 min 2. 25°, 18 h 3. Ac_2O, DMAP	 (46) + *cis*-β–anomer (30)	940, 942
		TMSOTf, MeCN, 0°, 10 min	 (80) α:β = 1:1	943
		TMSOTf, MeCN, 0°, 25 min	 (10) + β-isomer (8)	943
		TMSOTf, CH_2Cl_2, rt, 6 h	 (—)	944
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 6 h	 (70)	945
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 6 h	 (70)	945
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 3 d	 (—) α:β = 1:1	946
		TMSOTf, MeCN, 25°	 (79) R = 	947

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

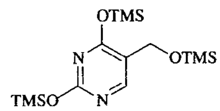
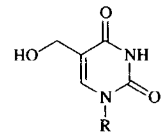
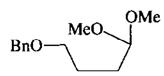
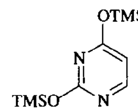
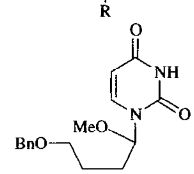
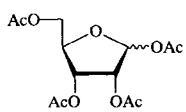
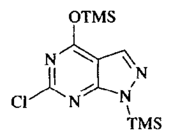
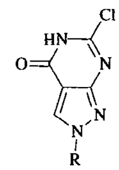
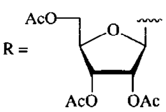
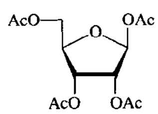
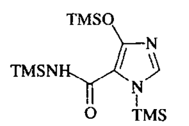
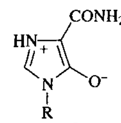
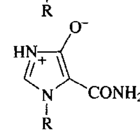
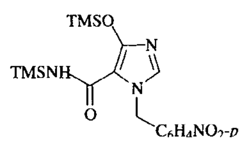
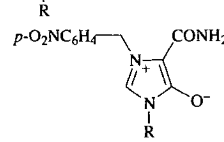
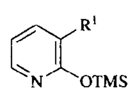
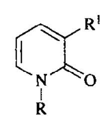
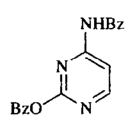
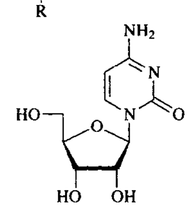
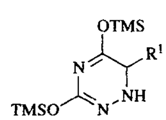
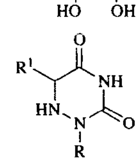
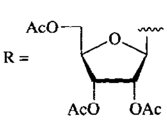
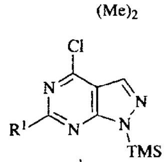
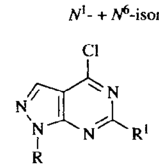
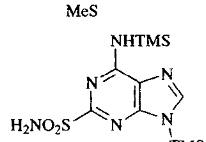
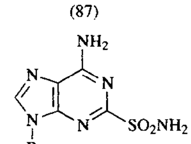
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, MeCN, 25°	 (66)	947
		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 (70)	923
		TMSOTf, MeCN, rt, 75 h	 (50) R = 	627
		TMSOTf, $Cl(CH_2)_2Cl$, $SnCl_4$, reflux, 1 h	 (83)	242
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1 h	 (61) + N^1-isomer (17) + bis(riboside) (9)	242
		TMSOTf, $Cl(CH_2)_2Cl$, $SnCl_4$, 60°, 1 h	 (76)	243
		TMSOTf, MeCN, rt, 15 h	 R^1: $CONH_2$ (50); CO_2Et (75)	948
		1. TMSOTf, $Cl(CH_2)_2Cl$, 0° 2. NH_4OH, MeOH, rt, 3 d	 (90)	424
		TMSOTf, $Cl(CH_2)_2Cl$, 60°, 15 min	 R = 	949a
	R^1			
	Me		N^1- + N^6-isomers (15), N^1:N^6 = 2:75	
	n-Pr		N^1- + N^6-isomers (6), N^1:N^6 = 1:1	
	$(Me)_2$		N^1- + N^6-isomers (40), N^1:N^6 = 0.7:1	
		TMSOTf, MeCN, rt, 16 h		
	R^1			
	Cl		(74)	627
	Me		(69)	949
	MeS		(87)	627
		TMSOTf, MeCN, rt, 5 h	 (53)	950

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

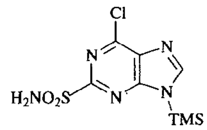
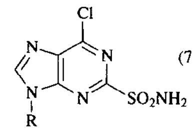
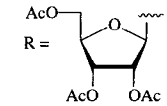
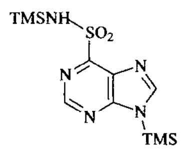
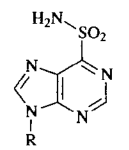
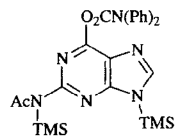
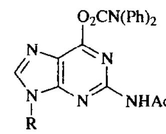
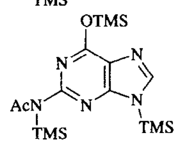
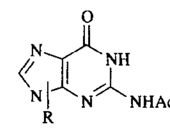
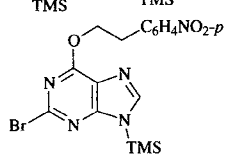
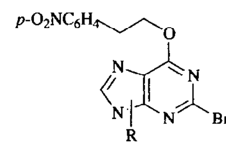
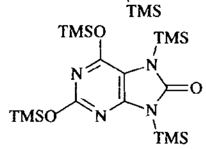
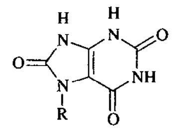
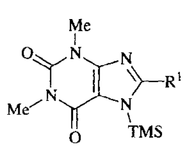
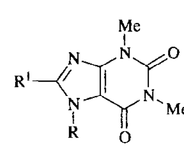
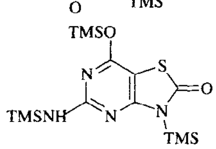
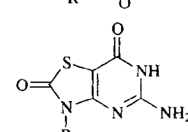
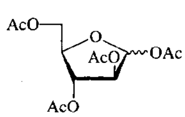
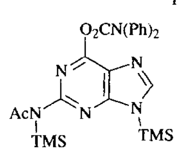
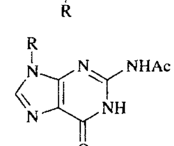
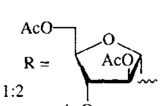
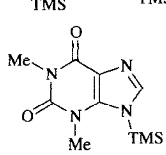
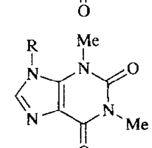
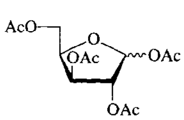
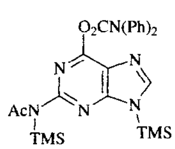
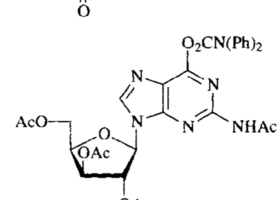
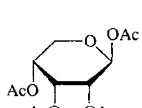
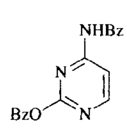
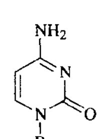
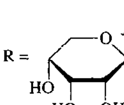
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, MeCN, rt, 2 h	 (71) R = 	950
		TMSOTf, MeCN, rt, 1 h	 (46)	951
		TMSOTf, PhMe, 80°, 1 h	 (91)	140
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1.5 h	 (81) N^7:N^9 = 1:3	142
		TMSOTf, MeCN, reflux, 1 h	 (95) N^7:N^9 = 1:20	143
		TMSOTf, $Cl(CH_2)_2Cl$, 5°, 72 h	 (81)	952
		TMSOTf, $Cl(CH_2)_2Cl$,	 R^1: H 50°, 1 h (91); Br 60°, 2 h (75)	953, 953
		TMSOTf, MeCN, rt, 12-16 h	 (29)	954
		TMSOTf, PhMe, 80°, 1 h	 (84) N^7:N^9 = 1:2 R = 	141
		TMSOTf, $Cl(CH_2)_2Cl$, 50°, 1 h	 (62)	368
		TMSOTf, PhMe, 80°, 1 h	 (67) N^7:N^9 = 1:2	141
		1. TMSOTf, $Cl(CH_2)_2Cl$, rt, 3 d 2. NH_4OH, MeOH	 (52) R = 	424

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

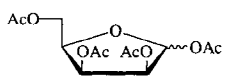
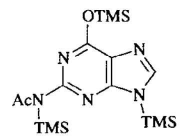
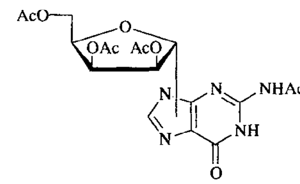
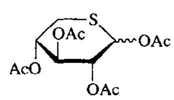
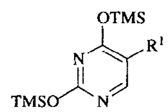
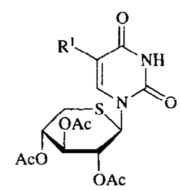
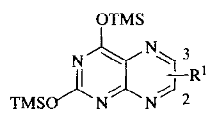
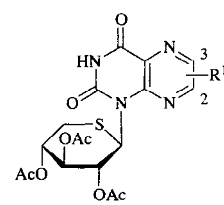
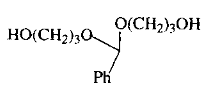
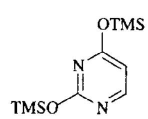
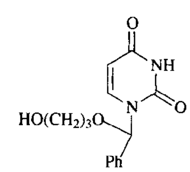
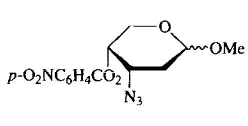
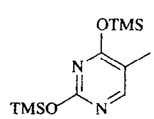
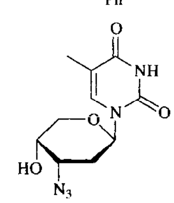
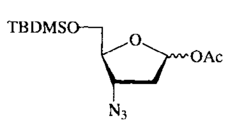
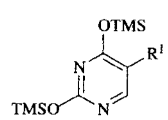
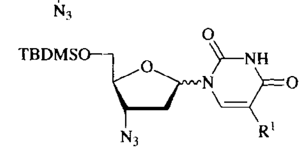
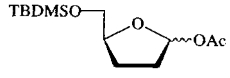
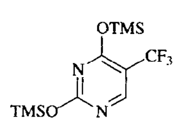
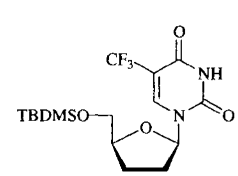
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1 h	 N^9 (59), N^7 (7)	537
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, time	 R^1 / time: F, 5 h (46); I, 6 h (52); Me, 3.5 h (50)	955
		TMSOTf		955
	R^1			
	3-C_6H_4Cl-*p*	CH_2Cl_2, rt, 6 h	(40)	
	2-C_6H_4Cl-*p*	CH_2Cl_2, rt, 7 h	(40)	
	3-C_6H_4Br-*p*	$Cl(CH_2)_2Cl$, rt, 48 h	(26)	
	2-C_6H_4Br-*p*	$Cl(CH_2)_2Cl$, rt, 24 h	(30)	
		TMSOTf, CH_2Cl_2, –30°, 2-12 h	 (51)	923
		1. TMSOTf, MeCN, 90°, 3 h 2. NaOMe, MeOH	 (63)	956
		TMSOTf		
	R^1		α:β	
	H	$Cl(CH_2)_2Cl$, rt, 18 h	(55) 1:2	280
	H	MeCN, rt, 24 h	(76) 1:1	749
	Me	$Cl(CH_2)_2Cl$, rt, 24 h	(66) 55:45	749
	Me	$Cl(CH_2)_2Cl$	(66) 1:1	280, 749
	Me	MeCN, rt, 24 h	(66) 53:47	749
		TMSOTf, –10°, 30 min	 (—)	292

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

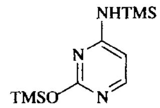
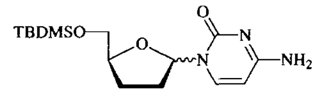
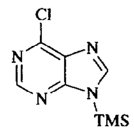
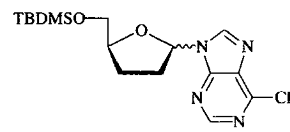
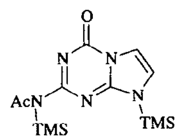
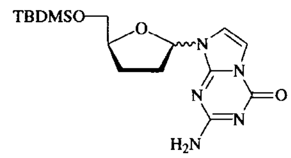
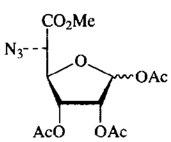
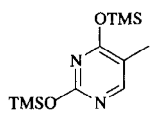
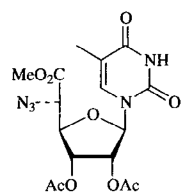
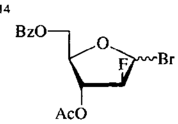
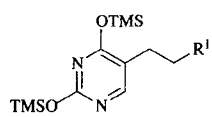
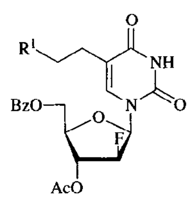
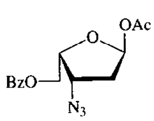
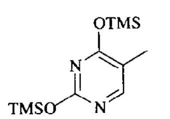
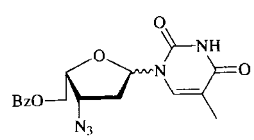
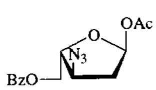
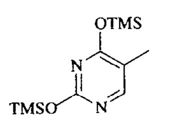
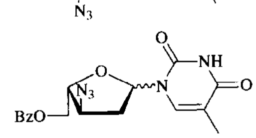
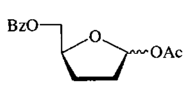
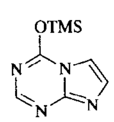
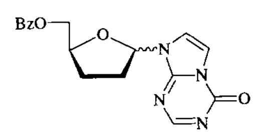
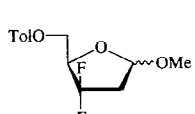
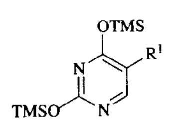
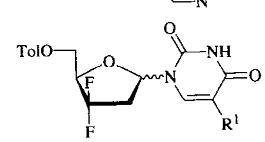
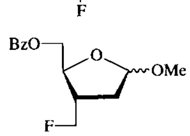
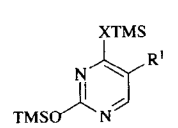
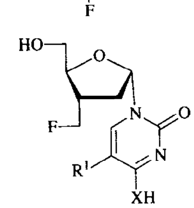
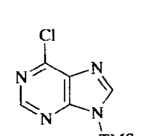
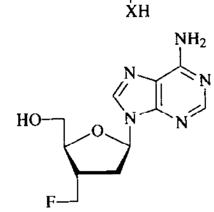
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$	 (—) α:β = 2:1	282
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 30 min	 (82) α:β = 1:1	298
		TMSOTf, MeCN, 25°, 4.5 h	 (56) α:β = 1:1	957
		TMSOTf, CH_2Cl_2, rt TMSOTf, $Cl(CH_2)_2Cl$, rt	 (93) (84)	958 959
C_{14} 		TMSOTf, MeCN, reflux, time	 R^1 / time: F, 1.5 h (25); Cl, 5 h (21)	360
		1. TMSOTf, MeCN, –35°, 45 min 2. rt, 30 min	 (58) α:β = 5:3	960, 961
		1. TMSOTf, MeCN, –30°, 20 min 2. rt, 30 min	 (72) α:β = 2:3	960
		TMSOTf, MeCN, 25°, 4 h	 (76) α:β = 1:1	957
		TMSOTf, MeCN, reflux, 3 h	 R^1 / α:β: H (26) 1:1; Me (31) 1:1	506
		1. TBDMSOTf, CH_2Cl_2, rt, 24 h 2. NH_3, MeOH, rt, 24 h	 R^1 / X / β-anomer: H, NH (38) (26); Me, O (36) (28)	962, 963
		1. TBDMSOTf, CH_2Cl_2, rt or 40°, 24 h 2. NH_3, MeOH, rt, 24 h or 100°, 20 h	 (39) + α-anomer (26)	962, 963

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

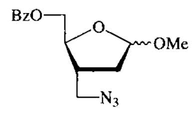
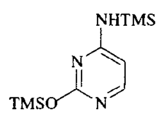
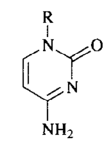
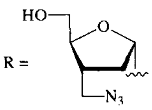
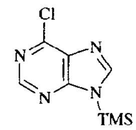
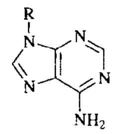
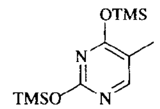
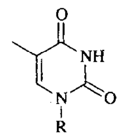
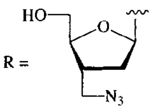
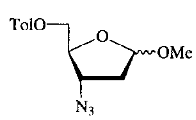
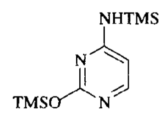
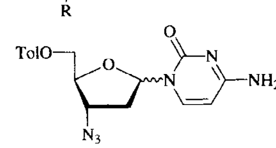
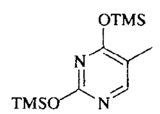
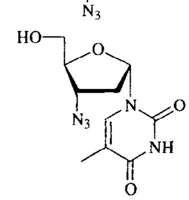
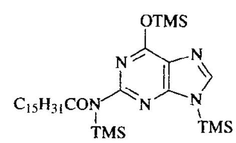
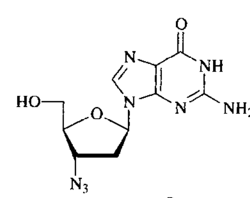
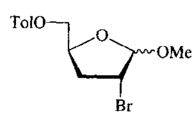
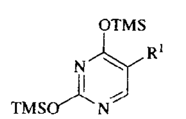
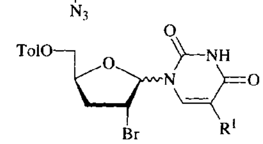
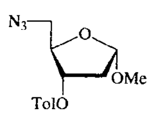
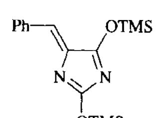
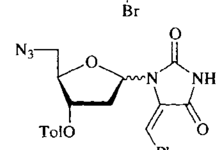
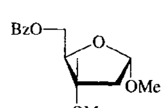
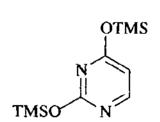
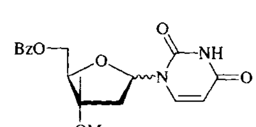
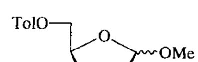
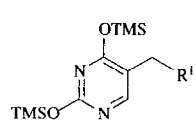
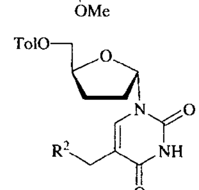
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. TBDMSOTf, CH_2Cl_2, rt, 24 h 2. NH_3, MeOH, rt, 24 h	 (43) + β-anomer (23) R = 	962, 963
		1. TBDMSOTf, CH_2Cl_2, rt, 24 h 2. NH_3, MeOH, rt, 24 h	 (17) + β-anomer (17)	962
		1. TBDMSOTf, CH_2Cl_2, rt, 24 h 2. NH_3, MeOH, rt, 24 h	 (30) + α-anomer (29) R = 	962, 963
		1. TBDMSOTf, CH_2Cl_2, reflux, 6 h 2. NH_3, MeOH, rt, 24 h	 (37)	279
		1. TBDMSOTf, CH_2Cl_2, reflux, 4 h 2. NH_3, MeOH, 20°, 18 h	 (32) + β-anomer (20)	279
		1. TBDMSOTf, CH_2Cl_2, reflux, 3 h 2. NH_3, MeOH, rt, 24 h	 (29)	279
		1. TMSOTf, MeCN, 0° 2. rt, time	 R^1 time H 12 h (63-68) F 4 h (63-68) Me 24 h (63-68)	964
		1. TMSOTf, MeCN, −50°, 5 min 2. −30°, 12 h	 (42) α:β = 1:1	965
		TMSOTf, $Cl(CH_2)_2Cl$	 (—) α:β = 1:1	966
	 R^1 OTMS OMe OBn	TMSOTf, CH_2Cl_2, 0°, 2-3 h	 R^2 β-anomer OH (18) (12) OMe (24) (16) OBn (24) (16)	967

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

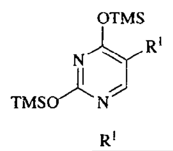
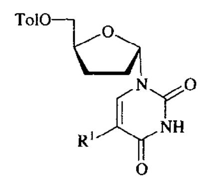
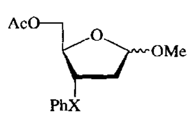
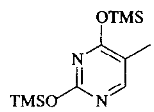
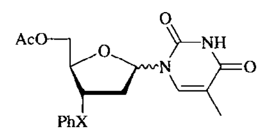
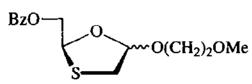
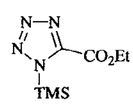
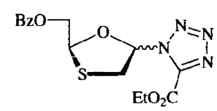
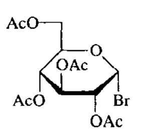
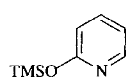
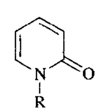
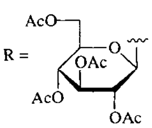
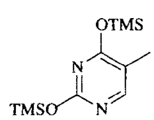
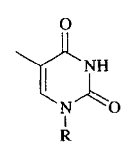
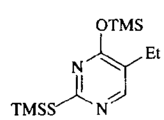
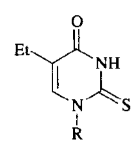
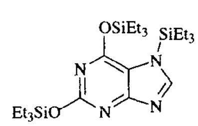
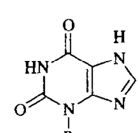
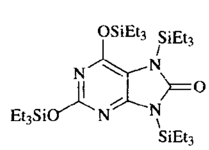
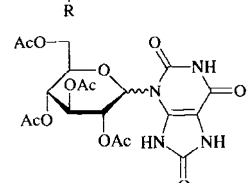
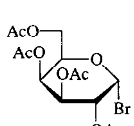
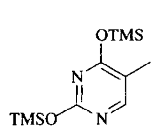
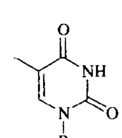
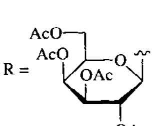
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
	 R^1 2-pyrrolidinyl N(Me)Bn N(Me)C_6H_{11} NHC_6H_4OEt-*o*	1. TMSOTf, MeCN, 0°, 15 min 2. rt, 0.5-3 h	 (yield) / β-anomer (37) (16) (—) (—) (22) (12) (—) (—)	968
		TBDMSOTf, CH_2Cl_2	 X S (30) Se (50)	969
		1. TMSOTf, MeCN, 0°, 5 h 2. rt, 15 h	 (50) α:β = 4:1	970
		$AgClO_4$, $MeNO_2$, 20°	 (70) R = 	74
		$AgClO_4$, C_6H_6, 20°, 0.25 h	 (61)	80
		$AgClO_4$, PhMe, 60°, 75 min	 (85)	971
		$AgClO_4$, PhMe, 70°	 (45)	74
		$AgClO_4$, PhMe, 20°	 (70)	74
		$AgClO_4$, C_6H_6, 20°, 16 h	 (50) R = 	80

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

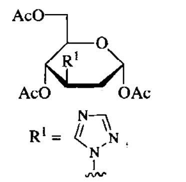
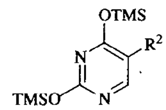
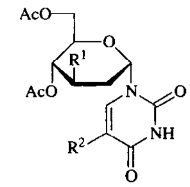
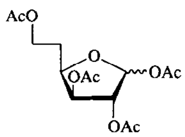
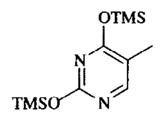
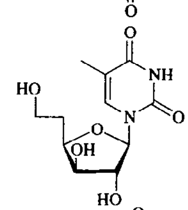
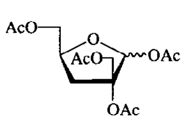
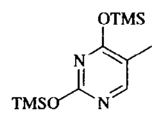
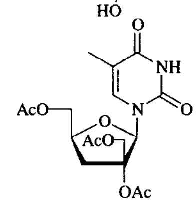
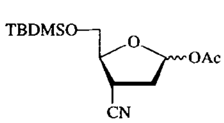
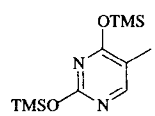
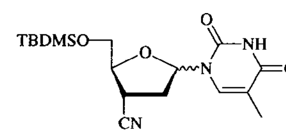
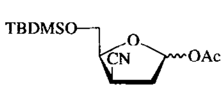
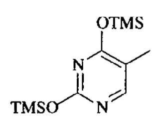
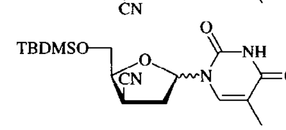
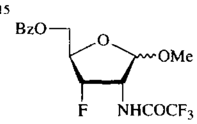
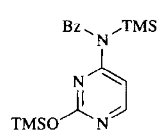
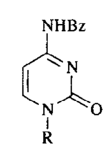
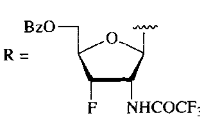
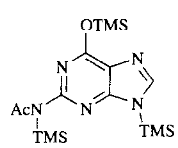
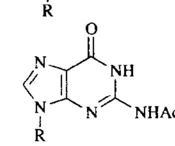
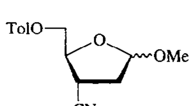
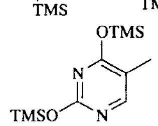
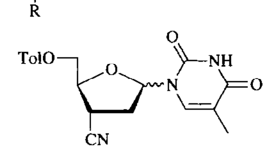
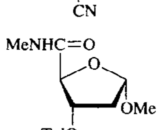
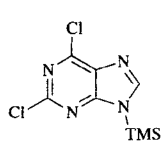
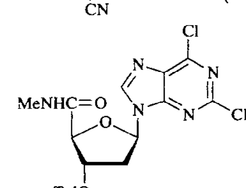
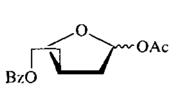
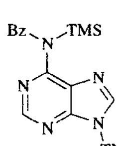
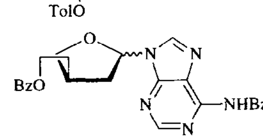
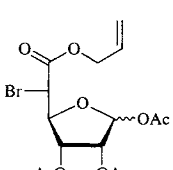
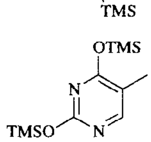
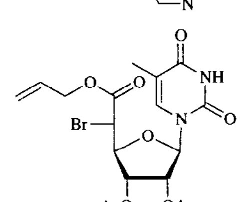
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. TMSOTf, MeCN, 0°, 1 h 2. rt, 23 h	 R^2 / β-anomer H (14) (8) Me (21) (9)	972
		1. TMSOTf, MeCN, rt, 4 h 2. NaOMe, MeOH, rt, 1 h	 (79)	937
		TMSOTf, MeCN, rt	 (50)	973
		TMSOTf, CH_2Cl_2, rt, 1 h	 (91) α:β = 5:4	114
		TMSOTf, CH_2Cl_2, rt, 1 h	 (50) α:β = 3:7	114
C_{15} 		TMSOTf, MeCN, reflux, 1.5 h	 (82) R = 	763
		TMSOTf, MeCN, reflux, 30 min	 (40) + N^7-isomer (20)	763
		TMSOTf, MeCN, reflux, 3 h	 (62) α:β = 1:1	287
		TMSOTf, CH_2Cl_2, rt, 16 h	 (64) α:β = 1:1	909[a]
		TMSOTf, MeCN, 4 h	 (35) α:β = 3:2	974
		TMSOTf, MeCN, 60°, 18 h	 (75)	975

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

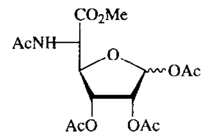
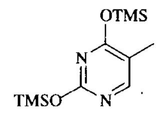
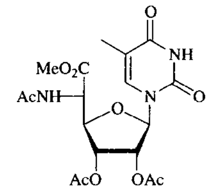
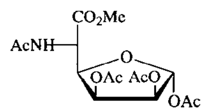
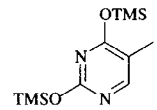
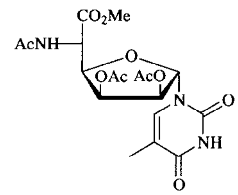
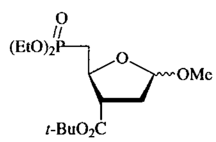
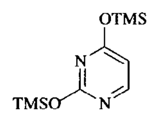
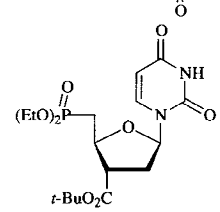
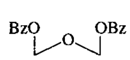
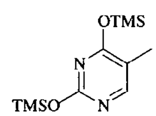
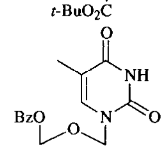
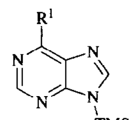
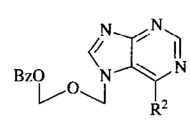
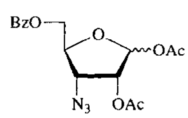
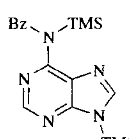
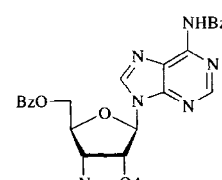
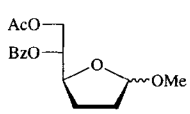
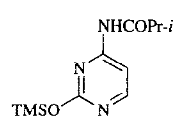
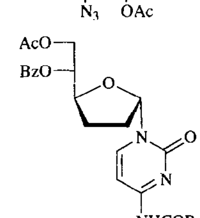
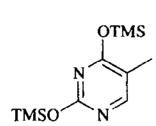
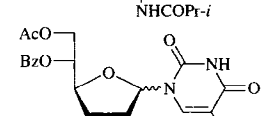
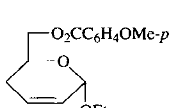
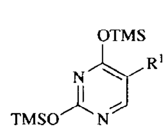
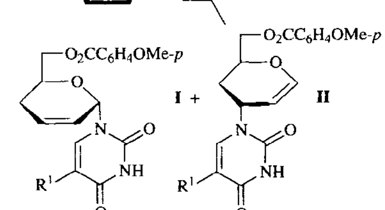
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$, reflux	 (23)	789
		TMSOTf, $Cl(CH_2)_2Cl$, 95°	 (79)	789
		1. TMSOTf, MeCN, 10°, 0.5 h 2. rt, 24 h	 (19) + α-anomer (12)	976
C_{16}				
		TMSOTf, CH_2Cl_2, 0 or 25°, 8 h	 (45-50)	650, 977
		TMSOTf, CH_2Cl_2, 0°	 R^1 / R^2: Cl / Cl (42); NHTMS / NH_2 (39)	977
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 5 h	 (77)	979
		1. TMSOTf, MeCN, 0°, 20 min 2. 20°, 30 min	 (45) + β-anomer (18)	980
		TMSOTf, MeCN, 0°, 2 h	 (37) α:β = 3:2	980
		TMSOTf, MeCN		311
	R^1			
	H	15 min	I (36) + β-anomer (8) + II (24)	
	Me	0°, 30 min	I (23) + β-anomer (13) + II (11)	

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

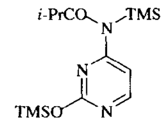
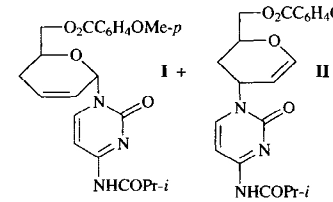
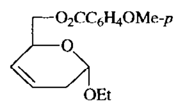
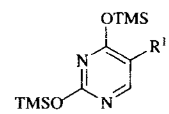
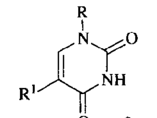
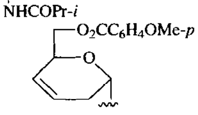
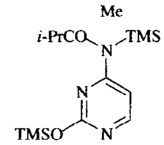
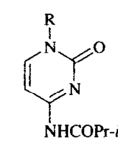
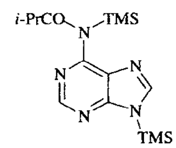
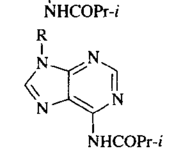
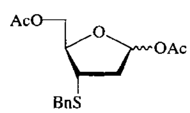
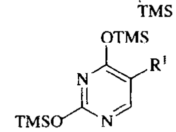
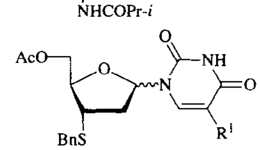
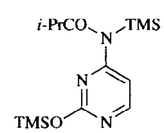
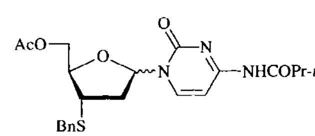
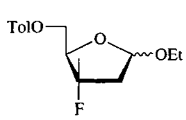
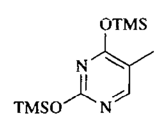
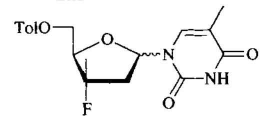
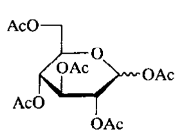
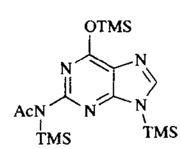
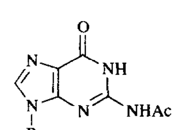
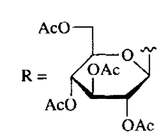
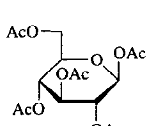
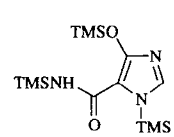
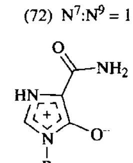
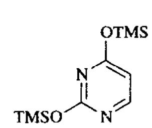
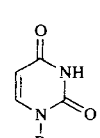
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, MeCN, 0°, 2 h	 I + II (—) I:II = 59:41	311
		TMSOTf, MeCN, rt, time	 R = 	311
	R^1: H	time: 5 h	(37), β-anomer (36)	
	R^1: Me	time: 2 h	(22), β-anomer (15)	
		TMSOTf, MeCN, rt, 3 h	 (23) + β-anomer (19)	311
		TMSOTf, MeCN, 0°, 4 h	 (13) + β-anomer (8)	311
		TMSOTf, MeCN, –30°, 2 h	 R^1: H (57); Me (33)	933
		TMSOTf, MeCN, –30°, 2 h	 (30)	933
		TMSOTf, MeCN, rt, 2.5 h	 (63)	981
		TMSOTf, Cl(CH$_2$)$_2$Cl, reflux, 16 h	 R =  (72) N^7:N^9 = 1:2	142
		TMSOTf, Cl(CH$_2$)$_2$Cl, SnCl$_4$, reflux, 1 h	 I (65)	242
		TMSOTf, Cl(CH$_2$)$_2$Cl, reflux, 1 h	I (22) + N^3-isomer (49) + bis(glucoside) (14)	242
		TMSOTf, Cl(CH$_2$)$_2$Cl, reflux, 2.5 h	 (92)	133

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

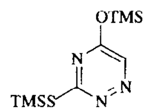
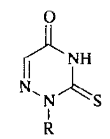
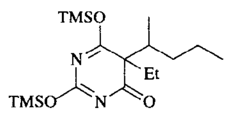
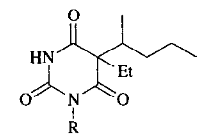
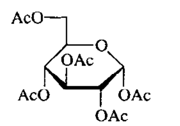
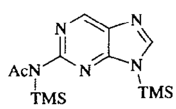
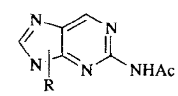
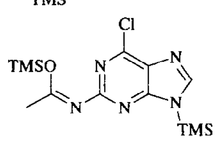
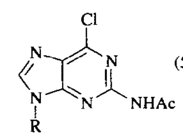
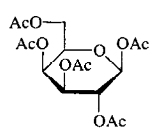
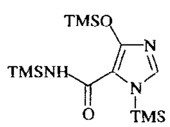
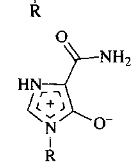
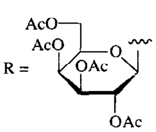
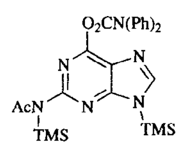
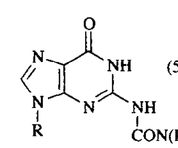
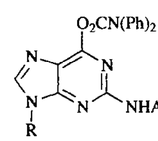
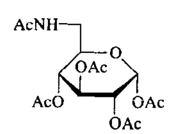
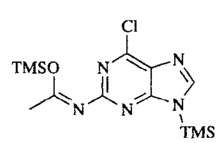
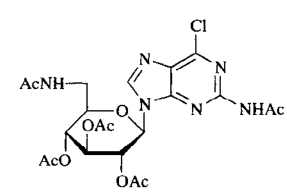
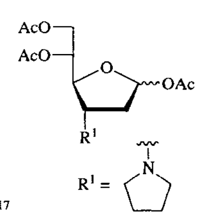
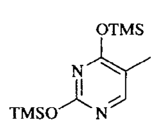
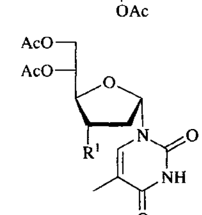
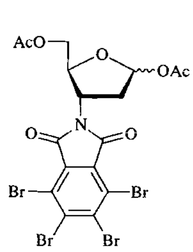
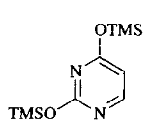
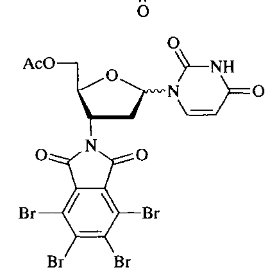
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$, C_6H_6, reflux, 3.5 h	 (65)	133
		TMSOTf, $Cl(CH_2)_2Cl$, CH_2Cl_2, rt, 18 h	 (59)	982
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 16 h	 (51) N^9:N^7 = 96:4	409
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1 h	 (56) + N^7-isomer (11)	409
		TMSOTf, $Cl(CH_2)_2Cl$, $SnCl_4$, reflux, 1 h	 I (67) R = 	242
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1 h	I (6) + N^3-isomer (47) + bis(glucoside) (10)	242
		TMSOTf, PhMe, 80°	 (52) +  (35)	143a
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 5-16 h	 I (48) + N^7-isomer (16)	409
C_{17} 		1. TMSOTf, $Cl(CH_2)_2Cl$, –20°, 1 h 2. $NaHCO_3$, H_2O	 (37) + β-anomer (34)	520
		1. TMSOTf, MeCN, 0°, 15 min 2. rt, 2 h	 (54)	983

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

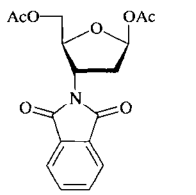
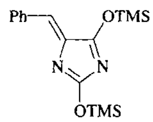
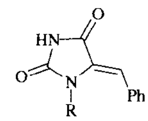
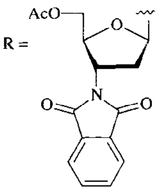
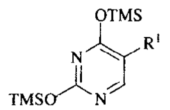
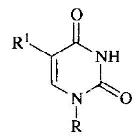
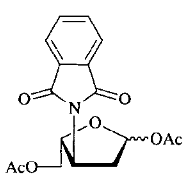
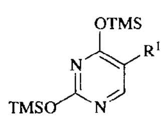
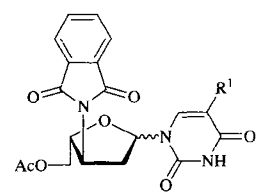
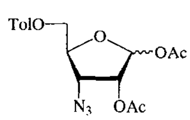
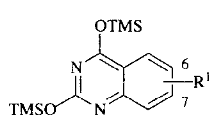
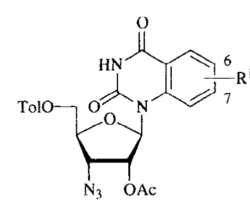
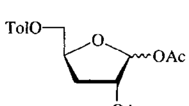
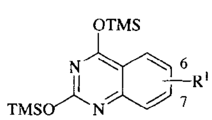
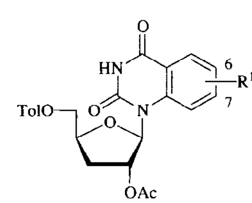
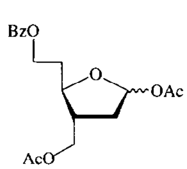
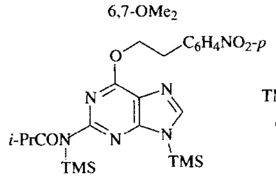
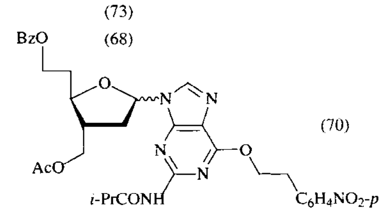
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. TMSOTf, MeCN, –50°, 5 min 2. –30°, 12 h	 R =  (45) + α-anomer (44)	965
		TMSOTf, MeCN, –30°, time		
	R^1	time		
	Cl	2 h	(40) + α-anomer (11)	984
	Me	2 h	(17)	984
	Me	2 h	(39) + α-anomer (24)	985
	CH_2OTMS	2 h	(30) α:β = 2:3	986
	CH_2OMe	2 h	(30)	986
	CH_2OBu-*s*	2-3 h	(26)	986
	$CH_2O(CH_2)_2OBu$-*n*	2-3 h	(22)	986
	$CH_2OC_{10}H_{21}$-*n*	2-3 h	(35)	986
	CH_2OBn	2-3 h	(28) + α-anomer (16)	986
		TMSOTf, MeCN, –30 to 0°, 3 h	 R^1 / α:β H (92) 1:2 Cl (81) 1:1 Me (92) 2:3	987
		TMSOTf, $Cl(CH_2)_2Cl$, 75°, 3 h		988
	R^1			
	H		(73)	
	6-Cl		(64)	
	6-Me		(73)	
	7-Me		(23)	
	6,7-Me_2		(39)	
	6,7-OMe_2		(26)	
		TMSOTf, $Cl(CH_2)_2Cl$, rt		989
	R^1			
	H		(59)	
	6-Me		(62)	
	7-Me		(67)	
	6,7-Me_2		(73)	
	6,7-OMe_2		(68)	
		TMSOTf, MeCN, 60°, 18 h	 (70)	990

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

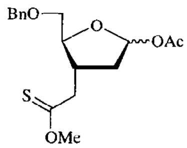
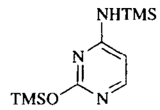
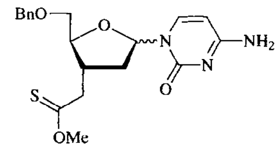
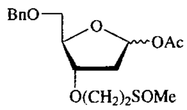
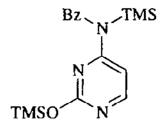
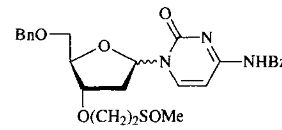
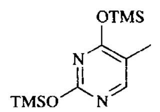
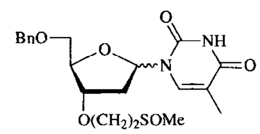
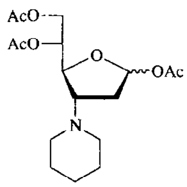
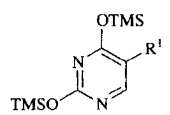
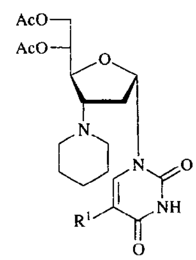
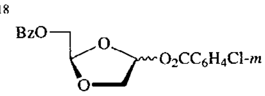
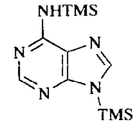
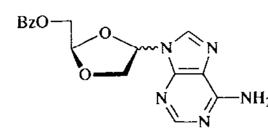
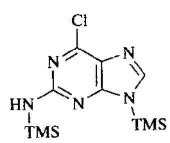
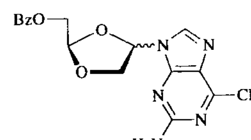
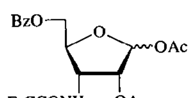
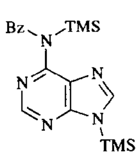
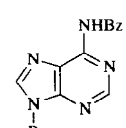
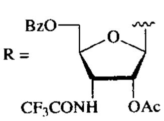
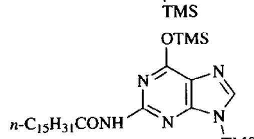
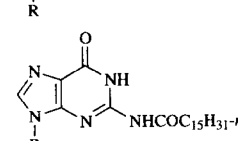
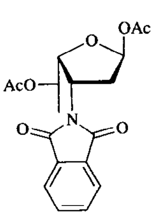
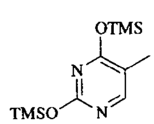
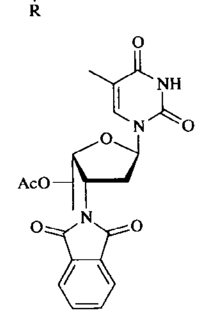
Sugar	Base	Conditions	Product(s) and Yield(s) (%)		Refs.
		TMSOTf, MeCN, rt		I (—) α:β = 24:76	278
		TMSOTf, $Cl(CH_2)_2Cl$, 40-50°	I (—) α:β = 23:77		278
		TMSOTf, CH_2Cl_2, −23°		(89) α:β = 25:75	277
		TMSOTf, CH_2Cl_2, −23°		I (89) α:β = 11:89	277
		TMSOTf, CH_2Cl_2, 0°, 15 min	I (96)		991
		TMSOTf, $Cl(CH_2)_2Cl$			520
	R^1			β-anomer	
	H	0°, 1 h	(40)	(34)	
	Me	−20°, 1 h; 0°, 1 h	(38)	(31)	
C_{18} 		TMSOTf, DMF, 120°		(—)	992
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 4 h		(—) α:β = 1:1	992
		TMSOTf, $Cl(CH_2)_2Cl$, PhMe, reflux, 1 h	 (80)	R = 	993
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 6 h	 (73)		994
		TMSOTf, MeCN, −35°, 15 min	 (54)		995

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

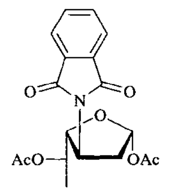
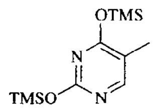
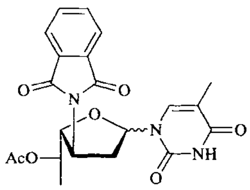
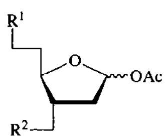
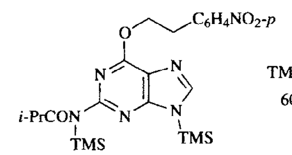
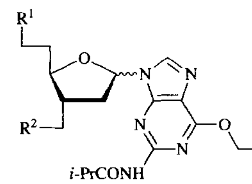
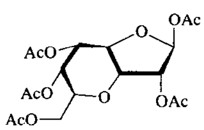
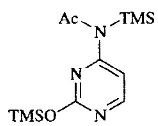
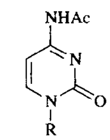
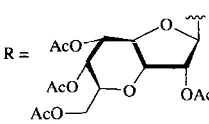
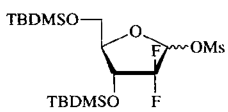
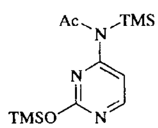
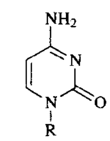
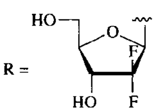
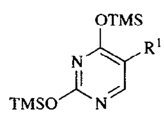
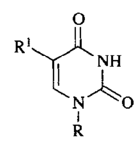
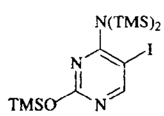
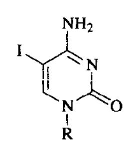
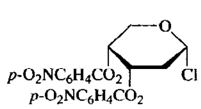
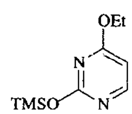
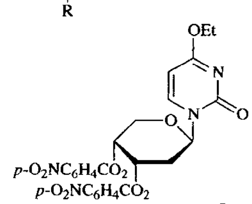
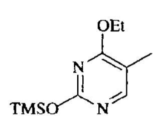
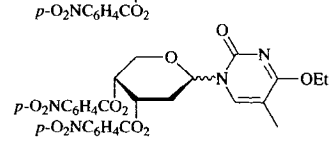
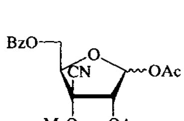
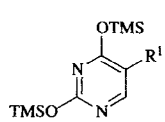
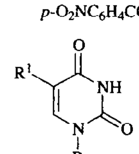
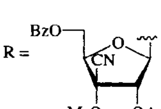
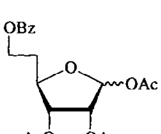
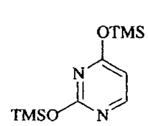
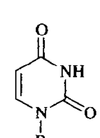
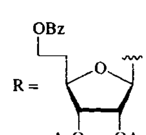
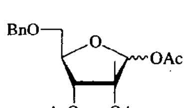
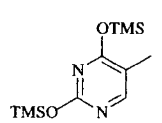
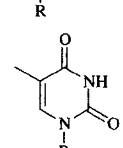
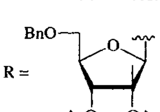
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, MeCN, −15°, 30 min	 (75) α:β = 1.76:2	995
		TMSOTf, MeCN, 60°, 18 h	 R^1 / R^2: OBz / OAc (—); OAc / OBz (—)	990
		TMSOTf, MeCN, rt, 5 h	 (53) R = 	158
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 3-15 h 2. NH_3, MeOH	 (10) + α-anomer (40) R = 	302, 996
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 2-15 h 2. HBr, CH_2Cl_2	 R^1: F (—); Me (—)	302, 996
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 3-15 h 2. HBr, CH_2Cl_2	 (—)	996
		$AgClO_4$	 (35) + α-anomer (55)	997
		$AgClO_4$	 (78)	998
		TMSOTf, MeCN, reflux, 3 h	 R^1: H (78); Me (77); Et (93) R = 	999
C_{19} 		TMSOTf, $Cl(CH_2)_2Cl$, 20°, 16 h	 (91) R = 	821
		TMSOTf	 (50) R = 	973

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

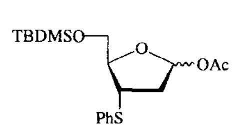
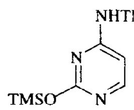
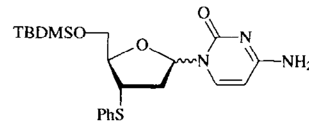
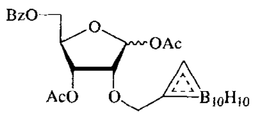
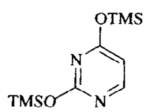
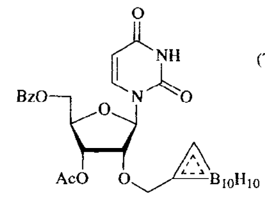
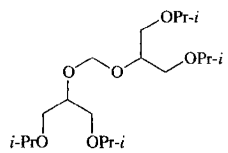
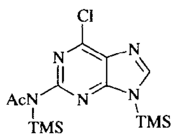
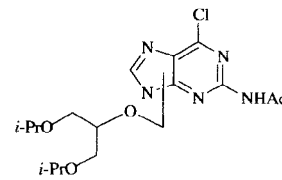
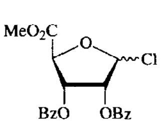
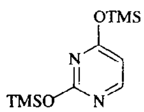
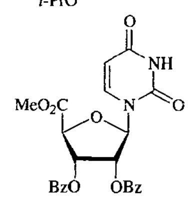
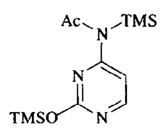
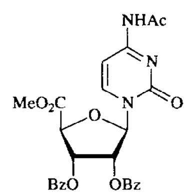
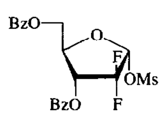
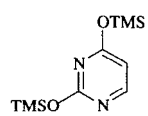
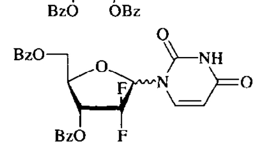
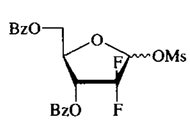
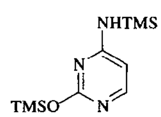
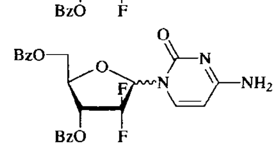
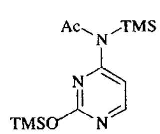
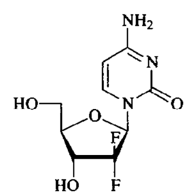
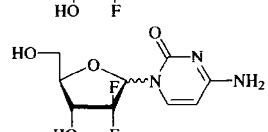
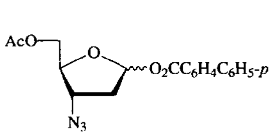
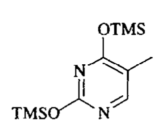
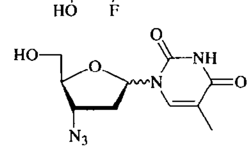
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$	 (—) α:β = 1:1	282
		TMSOTf, MeCN, rt, 4 h	 (71)	1000
		TMSOTf, $Cl(CH_2)_2Cl$, −30°, 2 h	 (58) N^7:N^9 = 10:1	521
C_{20} 		$AgClO_4$, C_6H_6, 25°, 18 h	 (64)	224
		$AgClO_4$, C_6H_6, 25°, 17 h	 (71)	224
		TMSOTf, $Cl(CH_2)_2Cl$, 83°, 5 h	 (—) α:β = 1.43:1	303
		TMSOTf, $CHCl_2CH_2Cl$ 113°, 18 h	 (87) α:β = 56:44	303
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 8 h 2. NH_3, MeOH	 (—) α:β = 1:1	1001
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 12 h 2. NH_3, MeOH	 (49) α:β = 53:47	303
		1. TMSOTf, MeCN, 2. $MeNH_2$, MeOH	 (—)	961

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

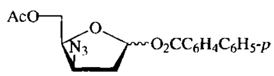
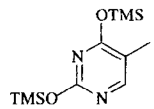
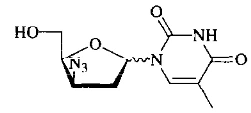
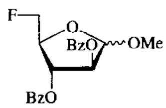
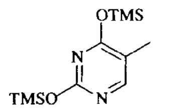
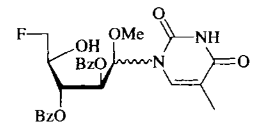
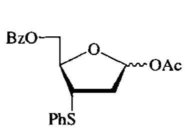
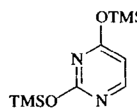
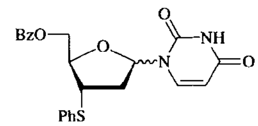
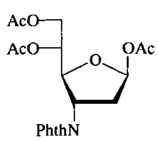
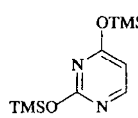
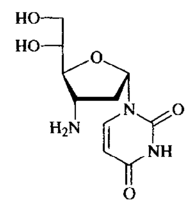
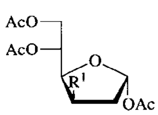
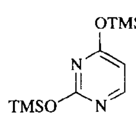
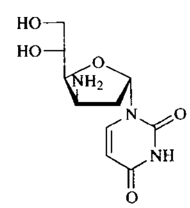
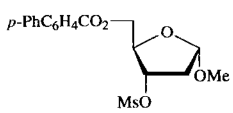
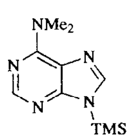
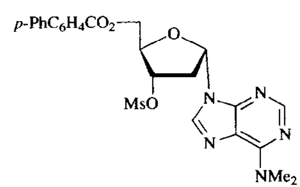
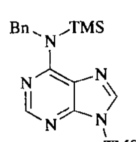
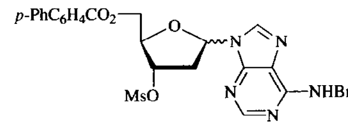
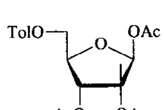
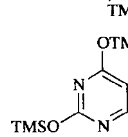
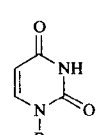
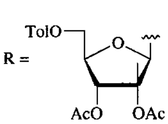
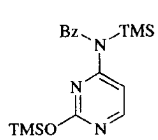
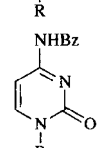
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. TMSOTf, MeCN 2. $MeNH_2$, MeOH	 (—)	961
		TMSOTf, MeCN, rt, 5 d	 (44)	925
		TMSOTf, CH_2Cl_2, $Sn(OTf)_2$, rt, 12 h	 **I** (78) $\alpha:\beta = 63:37$	229
		TMSOTf, CH_2Cl_2, $HgBr_2$, rt, 12 h	**I** (61) $\alpha:\beta = 69:31$	229
		TMSOTf, CH_2Cl_2, rt, 12 h	**I** (87) $\alpha:\beta = 60:40$	229
		1. TMSOTf, MeCN 2. $MeNH_2$, EtOH	 (—)	530
 R^1 = N(Phth)		1. TMSOTf, MeCN 2. $MeNH_2$, EtOH	 (—)	530
		TMSOTf, MeCN, –30°, 2 h	 (18) + α-anomer (21)	1002
		TMSOTf, MeCN, –30 to 20°, 18 h	 (15) $\alpha:\beta = 3:1$	1003
		TMSOTf, $Cl(CH_2)_2Cl$, 20°, 16 h	 (89) R = 	1004
		TMSOTf, $Cl(CH_2)_2Cl$, 20°, 16 h	 (65)	1004

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

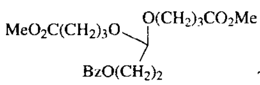
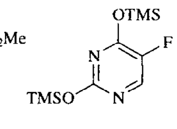
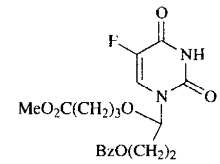
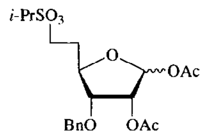
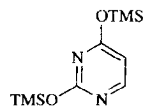
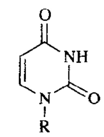
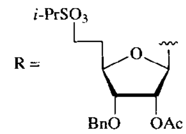
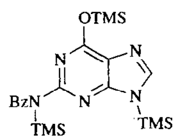
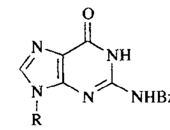
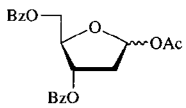
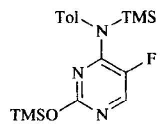
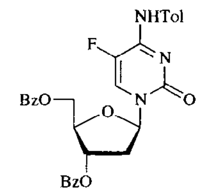
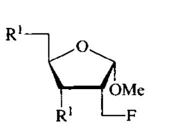
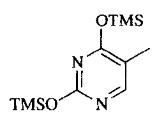
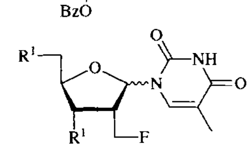
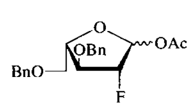
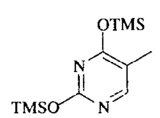
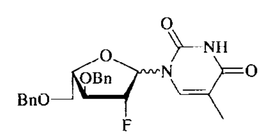
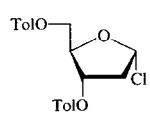
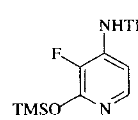
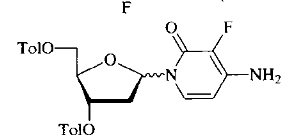
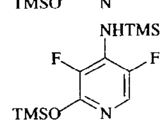
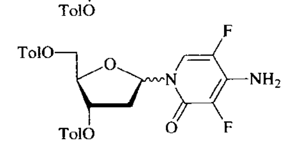
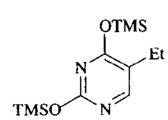
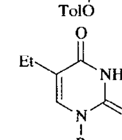
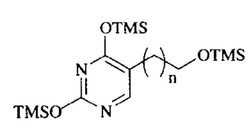
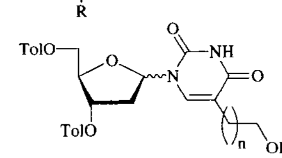
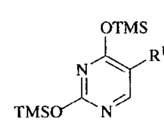
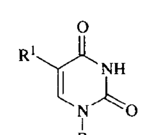
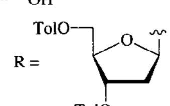
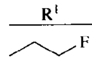
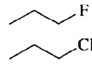
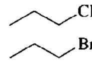
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, CH_2Cl_2, −30°, 2-12 h	 (62)	923
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 20 h	 (75) R = 	508
		TMSOTf, $Cl(CH_2)_2Cl$, 40°, 4.5 h	 (35) + N^7-isomer (13)	508
		TMSOTf, MeCN, rt, 1.3 h	 (31) + α-anomer (18)	151
 $R^1 = Cl_2C_6H_3CH_2O$		TMSOTf, MeCN, 50°	 (76) α:β = 1:2.7	689
		TMSOTf	 (—)	978
		1. TMSOTf, $Cl(CH_2)_2Cl$, −25°, 30 min 2. rt, 24 h	 (83)	860, 861
		1. TMSOTf, $Cl(CH_2)_2Cl$, 0°, 30 min 2. rt, 24 h	 (82) α:β = 1:1	860
		TMSOTf, $Cl(CH_2)_2Cl$, 24°, 3 h	 (58) + α-anomer (32)	133
		TMSOTf, $CHCl_3$, rt, 1 h	 n / β:α — 1: (84) 5:1; 2: (—) —	1005
		TMSOTf, $CHCl_3$, rt, 1 h	 R = 	
	R^1		(α-anomer)	
			(72) (10)	360
			(65) (15)	1005
			(71) (15)	1005

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

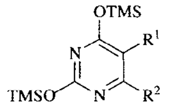
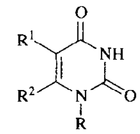
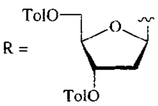
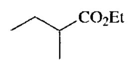
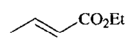
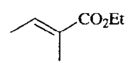
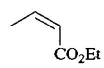
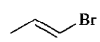
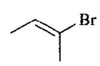
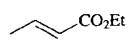
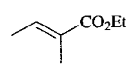
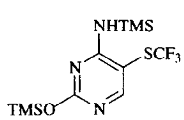
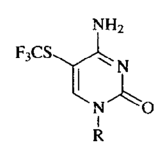
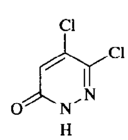
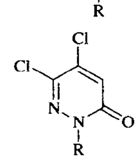
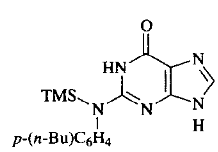
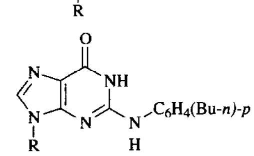
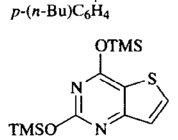
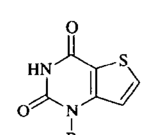
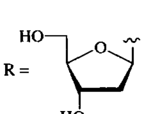
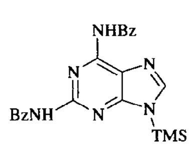
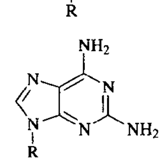
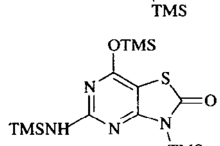
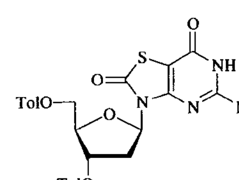
Sugar	Base		Conditions	Product(s) and Yield(s) (%)		Refs.
			1. TMSOTf, $CHCl_3$, rt 2. NaOEt, EtOH		R = 	
	R^1	R^2			α-anomer	
		H	1 h	(17)	(18)	1006
		H	—	(61)	(37)	1006
		H	—	(74)	(—)	1006
		H	—	(61)	(—)	1006
		Me	—	(10)	(—)	1006
		H	—	(31)	(—)	1006
		Me	—	(25)	(—)	1006
		H	—	(74)	(—)	1006
	SCF_3	H	62°, 4 h	(85)	(—)	1007, 1008
	SO_2CF_3	H	62°, 3 h	(89)	(—)	1007
	$SeCF_3$	H	62°, 4 h	(84)	(—)	1007
			TMSOTf, dioxane, 90°, 4 h	 (67)		1007
			TMSOTf, MeCN, rt, 2 h	 (67) + α-anomer (12)		1009
			TMSOTf, $Cl(CH_2)_2Cl$, C_6H_6, rt to reflux, 2 h	 (18) + N^7 β-isomer (16) + N^7 α-isomer (6)		505
			1. TMSOTf, $CHCl_3$, rt, 3 h 2. NH_3, MeOH	 (65) + α-anomer (35)	R = 	893
			1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 3 h 2. NaOMe	 (39)		1010
			TMSOTf, 110°, 30 min	 (14) α,β mixture		954

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

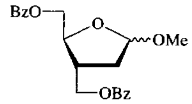
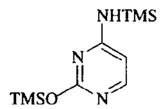
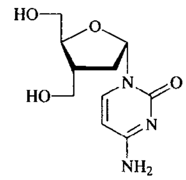
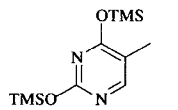
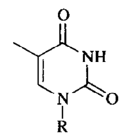
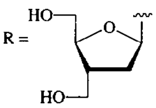
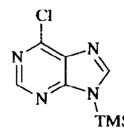
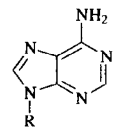
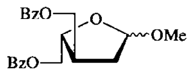
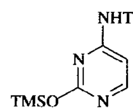
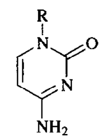
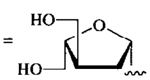
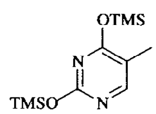
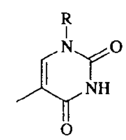
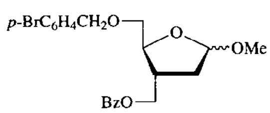
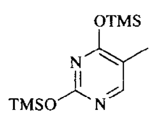
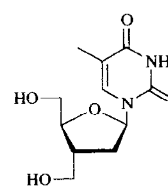
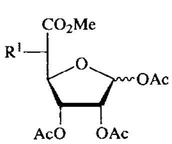
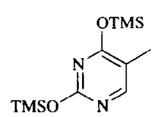
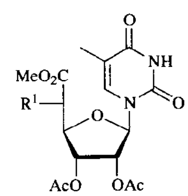
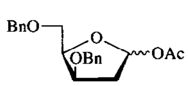
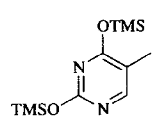
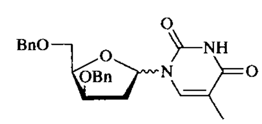
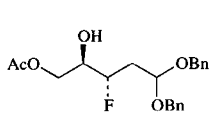
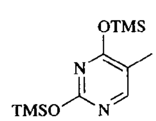
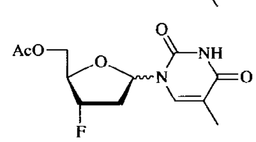
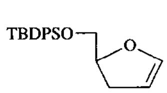
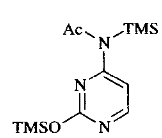
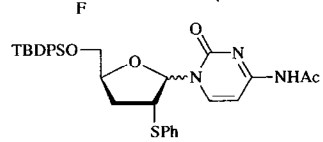
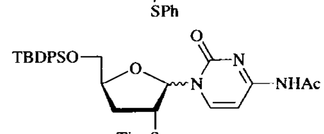
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. TBDMSOTf, CH_2Cl_2, rt, 24 h 2. NH_3, MeOH	 (30) + β-anomer (24)	963, 1011
		1. TBDMSOTf, CH_2Cl_2, rt, 24 h 2. NH_3, MeOH, reflux, 24 h	 (33) + α-anomer (33) R = 	1011
		1. TBDMSOTf, MeCN or CH_2Cl_2, rt, 24 h 2. NH_3, MeOH 100°, 20 h	 (20) + α-anomer (10)	1011, 963
		1. TBDMSOTf, CH_2Cl_2 2. NH_3, MeOH	 (24) + β-anomer (20) R = 	1012
		TBDMSOTf, CH_2Cl_2	 (41) + β-anomer (36)	1012
		1. TBDMSOTf, CH_2Cl_2, rt, 24 h 2. H_2, Pd/C 3. NH_3, MeOH	 (33) + α-anomer (33)	1011
		TMSOTf, $Cl(CH_2)_2Cl$, reflux	 R^1 CbzNH (82) CbzNH (75)	789, 1013 1014
		TMSOTf, CH_2Cl_2, rt, 1 h	 (87) α:β = 1:1	405
		TMSOTf, MeCN, 25°, 2.75 h	 (71) α:β = 1:2.8	300
		TMSOTf, PhSCl, CH_2Cl_2, –78 to 0°, 1.5 h	 (60) α:β = 1:5	421a
		TMSOTf, TippSCl, CH_2Cl_2, –78 to 25°, 2 h	 (75) α:β = 1:6	421a

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

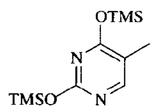
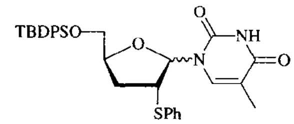
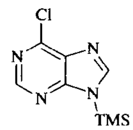
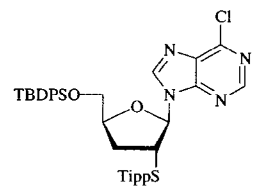
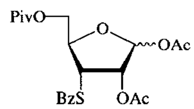
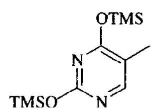
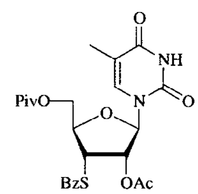
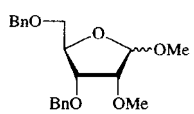
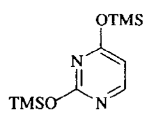
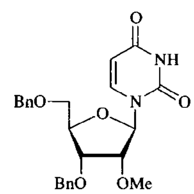
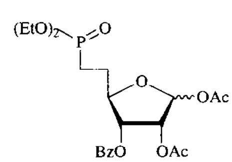
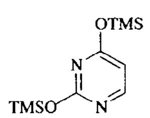
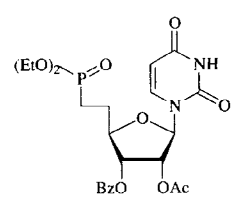
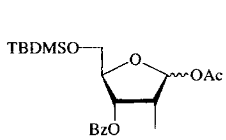
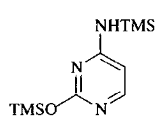
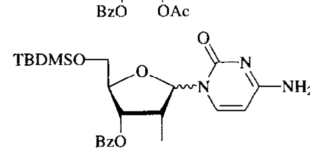
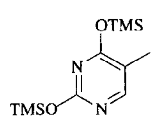
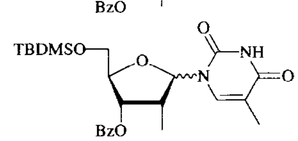
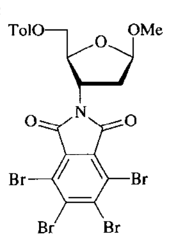
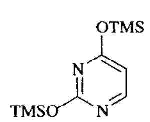
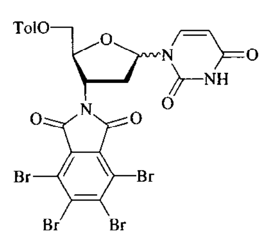
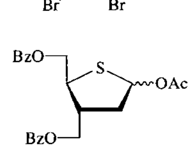
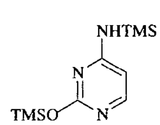
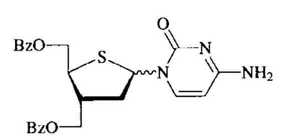
Sugar	Base	Conditions	Product(s) and Yield(s) (%)		Refs.
		TMSOTf, PhSCl, CH_2Cl_2, −78 to 0°, 1.5 h		(50) α:β = 1:4	421a
		TMSOTf, TippSCl, Et_2O, −78 to 25°, 2 h		(80) α:β = 1:5	421a
		TMSOTf, CH_2Cl_2, or MeCN, 70°		(85)	1015
		TMSOTf, MeCN, 25°, 2-3 h		(65) + α-anomer (11)	226b
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 16 h		(30) + N^7-ethyluracil (36)	821
		TMSOTf, MeCN, rt		(72) α:β = 1:9	829
		TMSOTf, $Cl(CH_2)_2Cl$, rt		(77) α:β = 1:6.7	829
C_{22} 		TMSOTf, MeCN, 0°, 15 min; rt, 2 h		(49)	983
		TBDMSOTf, MeCN, 0°, 1 h		(37)	963

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

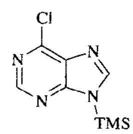
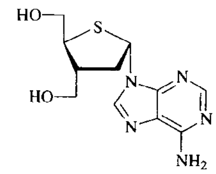
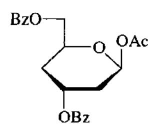
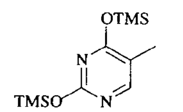
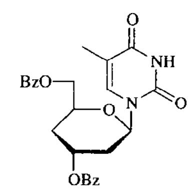
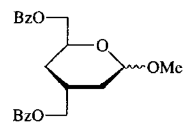
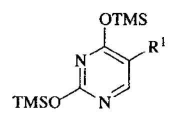
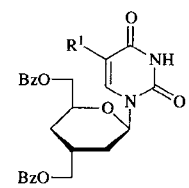
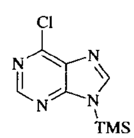
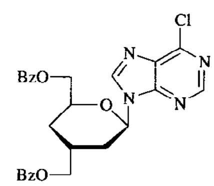
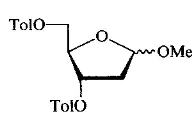
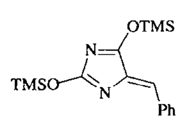
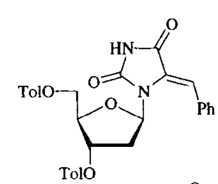
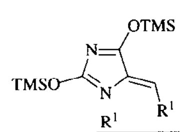
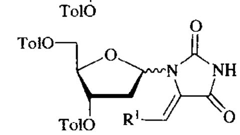
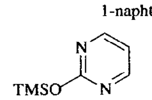
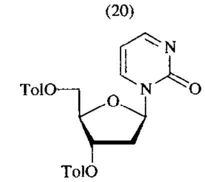
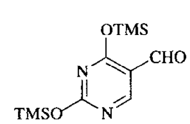
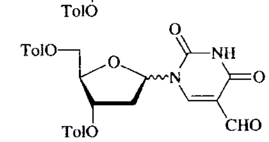
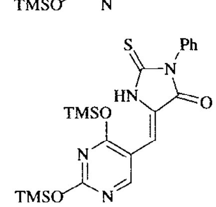
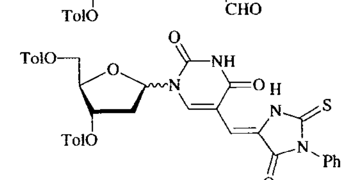
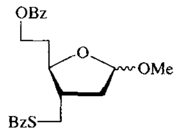
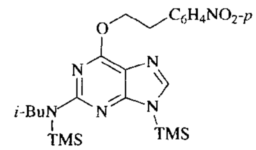
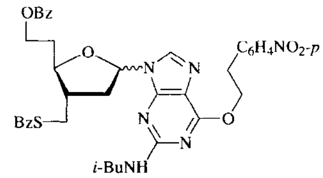
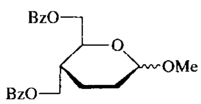
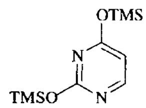
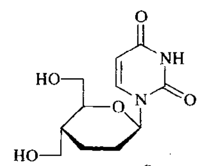
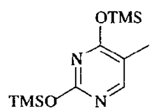
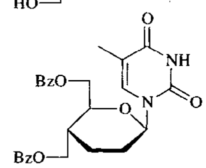
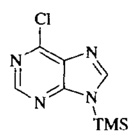
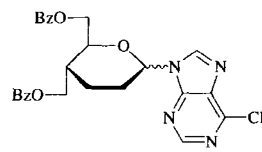
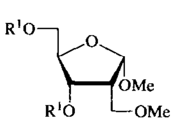
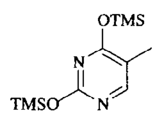
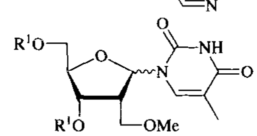
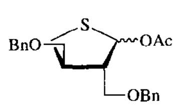
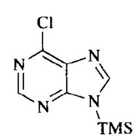
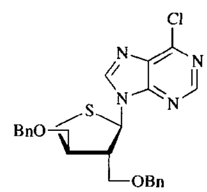
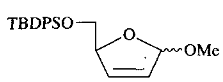
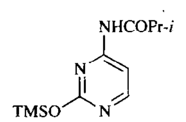
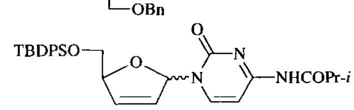
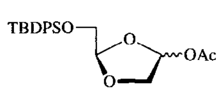
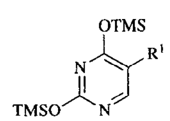
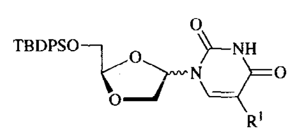
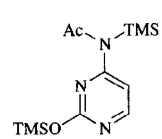
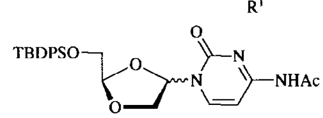
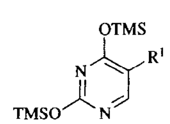
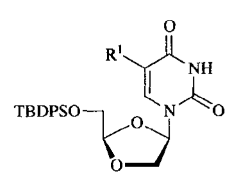
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. TMSOTf, CH_2Cl_2, rt, 24 h 2. NH_3, MeOH	 (33) + β-anomer (28)	1016
		TMSOTf	 (55) + α-anomer (22)	922
		TBDMSOTf, MeCN, CH_2Cl_2, rt, 15 h	 R^1: H (68); Me (72) α:β = 1:12	236
		TBDMSOTf, MeCN, CH_2Cl_2, rt, 15 h	 (68)	236
		TMSOTf, MeCN, –30°, 4 h; –10°, 3 d	 (55) + α-anomer (19)	1017
		TMSOTf, MeCN, –30°, 4 h; –10°, 3 d		1017
	R^1			
	Me		(63)	
	2-thienyl		(80) α:β = 1:2	
	2-naphthyl		(78)	
	1-naphthyl		(20)	
		TMSOTf, MeCN, 20°, 3 h	 (30)	147
		TMSOTf, MeCN, –50°, 2 h; –10°, 12 h; rt, 4 h	 (63) α:β = 1:2	1018
		TMSOTf, MeCN, –50°, 2 h; –10°, 12 h; rt, 12 h	 (46) α:β = 1:4	1018

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, MeCN, 60°, 18 h	 (—)	990
		1. TBDMSOTf, MeCN, CH_2Cl_2 2. NaOMe, MeOH	 (47)	236
		TBDMSOTf, MeCN, CH_2Cl_2, rt, 15 h	 (66) + α-anomer (6)	236
		TBDMSOTf, MeCN, CH_2Cl_2	 (68) α:β = 1:13	236
 $R^1 = Cl_2C_6H_3CH_2$		TMSOTf, $Cl(CH_2)_2Cl$, 50°	 (76) α:β = 1:3	829
		TMSOTf, CH_2Cl_2, rt, 3 h	 (85) α:β = 2.7:1	1019
		TMSOTf, MeCN, –20°, 2.5 h	 (49)	1020
		TMSOTf, $Cl(CH_2)_2Cl$, rt	 R^1: H 2 h (60); I 1 h (35); α:β = 1:1	1021
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 45 min	 (78) α:β = 1:1	1021
		TMSOTf		

R^1	Conditions	Product	α-anomer	Refs.
H	$Cl(CH_2)_2Cl$	(45)	(29)	1021
Cl	$Cl(CH_2)_2Cl$, rt, 1 h	(30)	(27)	1021
Br	$Cl(CH_2)_2Cl$, rt, 1 h	(35)	(30)	1021
Me	$Cl(CH_2)_2Cl$, rt, 1 h	(45)	(29)	1022

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

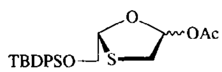
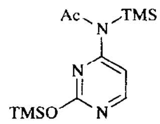
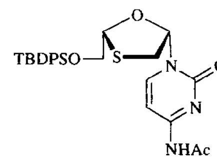
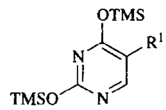
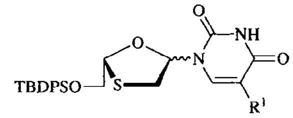
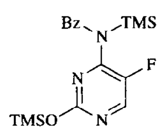
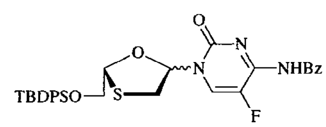
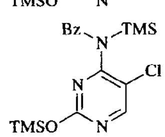
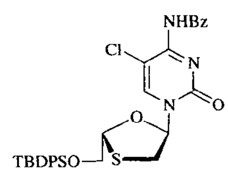
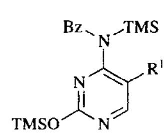
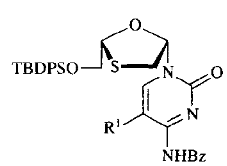
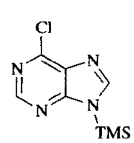
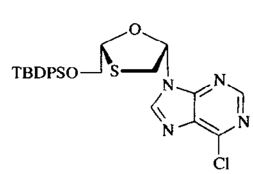
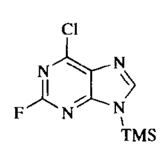
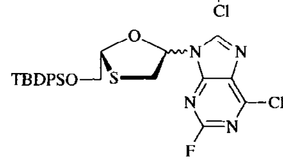
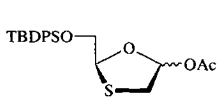
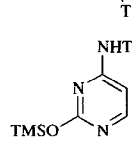
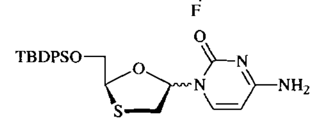
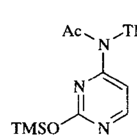
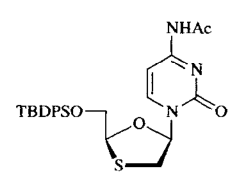
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$		
		0° to rt	(64)	249
		rt, 1.5 h	(45) + β-anomer (22)	1023
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 2 h		1023
	R¹			
	F		(93)	
	Cl		(58)	
	Br		(53)	
	I		(88)	
	Me		(72)	
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 2 h	 (42) + β-anomer (32)	1023
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 2 h	 (44) + α-anomer (30)	1023
		TMSOTf, $Cl(CH_2)_2Cl$, rt, time		1023
	R¹	time	NHBz / β-anomer	
	Br	1.5 h	(45) / (30)	
	I	1 h	(36) / (24)	
	Me	2 h	(35) / (28)	
		TMSOTf, CH_2Cl_2, rt, 30 min; reflux, 14 h	 (35) + β-anomer (30)	1023
		TMSOTf, CH_2Cl_2, rt, 16 h	 (60)	1023
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 45 min	 (—) α:β = 1:1	235
		TMSOTf, $Cl(CH_2)_2Cl$, 0° to rt	 (60)	1024

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

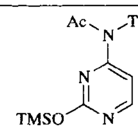
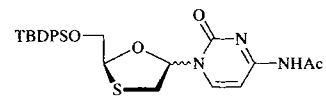
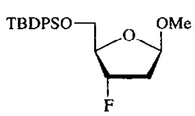
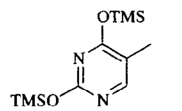
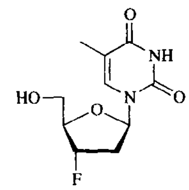
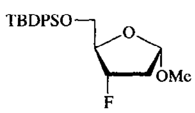
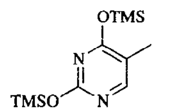
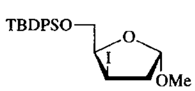
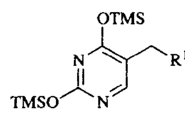
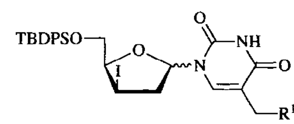
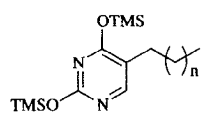
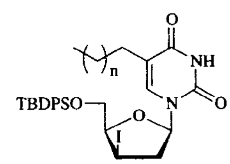
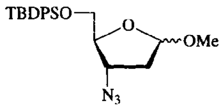
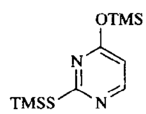
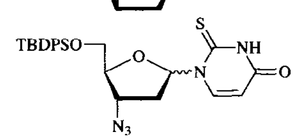
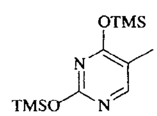
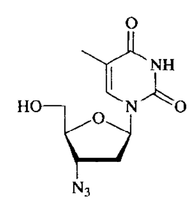
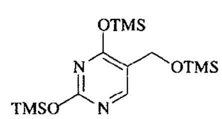
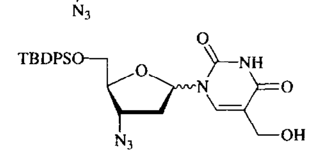
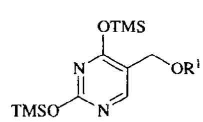
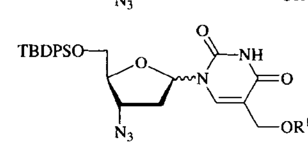
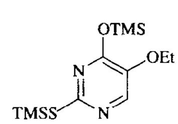
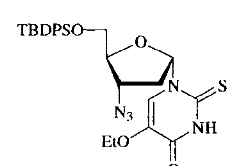
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$	 (50) α:β = 1:2	1025
		1. TMSOTf, MeCN, rt, 2.5 h 2. n-Bu_4NF, THF, rt, 1 h	 I (35) + α-anomer (35)	281
		1. TMSOTf, MeCN, rt, 40 min 2. n-Bu_4NF, THF, rt, 30 min	I (44) + α-anomer (20)	281
		TMSOTf, MeCN, −10°, 30 min; rt, 1-4 h	 R[1] — α:β H (70) 1:1 OMe (67) 1:1	1026
		TMSOTf, MeCN, −17°, 10-12 h	 n — — α-anomer 3 (16) (5) 4 (13) (9) 6 (32) (21)	1027
		TMSOTf, MeCN, 20°, 30 min	 (—) α:β = 2:1 α-anomer (16)	286
		1. TBDMSOTf, MeCN, rt, 1 h 2. F_3CCO_2H (50% aq), rt, 20 h	 I (33) + α-anomer (29)	281
		1. TMSOTf, MeCN, 5°, 3 h 2. $NaHCO_3$	 (74)	1028
		TMSOTf, MeCN, 5°, 3 h		
	R[1]			
	Me		(56)	1028
	Et		(83)	1028
	Pr-n		(79)	1028
	Bu-n		(69)	1028
	C_5H_{11}-n		(67)	1028
	C_6H_{13}-n		(36)	1028
		TMSOTf, MeCN, 5°, 3 h	 (15) α:β = 5:3	286

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

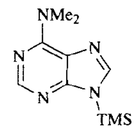
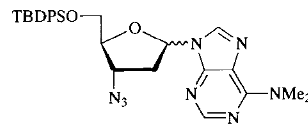
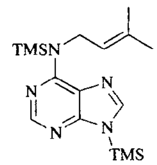
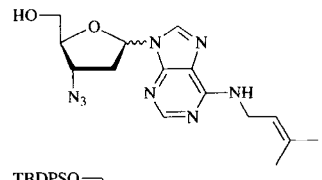
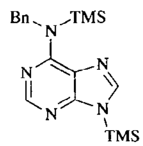
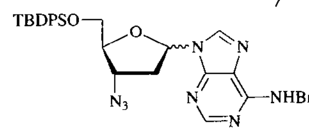
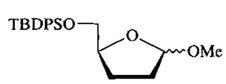
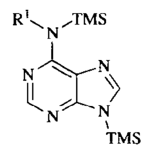
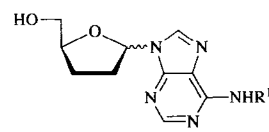
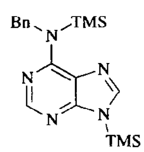
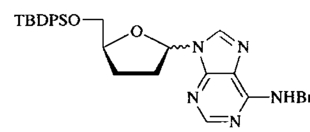
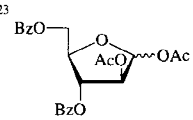
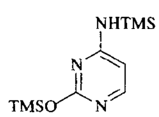
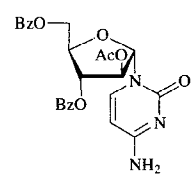
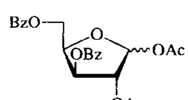
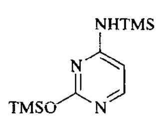
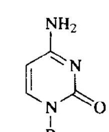
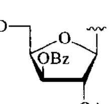
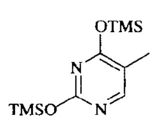
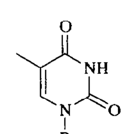
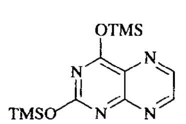
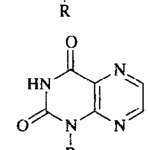
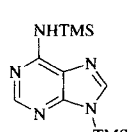
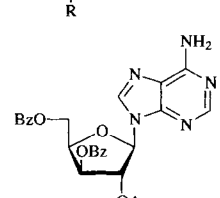
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, MeCN, −30 to 0°, 3 h	 (35) α:β = 4:1	1002
		1. TMSOTf, MeCN, −30 to 20°, 72 h 2. Bu_4NF, THF	 (14) + α-anomer (25)	1003
		TMSOTf, MeCN, −30 to 20°, 72 h	 (43) α:β = 1:1	1003
	 $R^1 = 3,4\text{-}Cl_2C_6H_3CH_2$	1. TMSOTf, MeCN, −30 to −10°, 4 h 2. Bu_4NF, THF	 (28) α:β = 2:1	1003
		TMSOTf, MeCN, −30 to −10°, 4 h	 (41) α:β = 1:1	1003
C_{23} 		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 16 h	 (56)	595
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1 h	 (75) R = 	537
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 5 h	 (57)	828
		TMSOTf, EtOAc, rt, 2 h	 (69)	1029
		1. TMSOTf 2. NH_2NH_2	 (70)	828

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

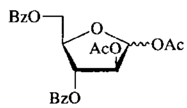
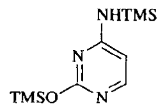
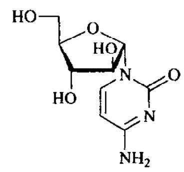
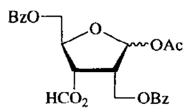
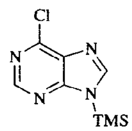
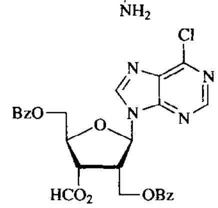
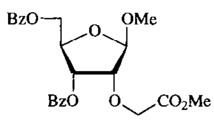
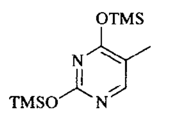
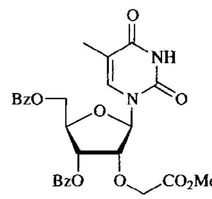
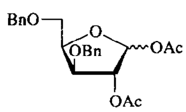
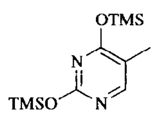
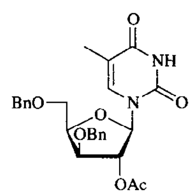
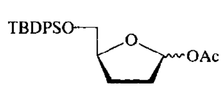
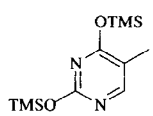
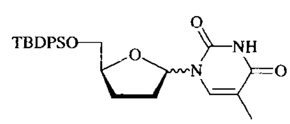
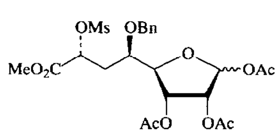
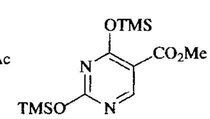
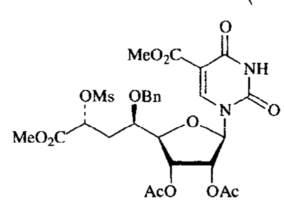
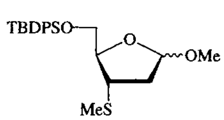
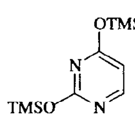
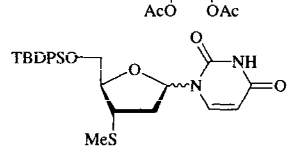
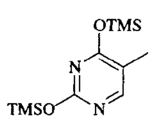
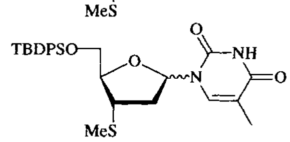
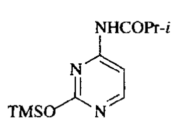
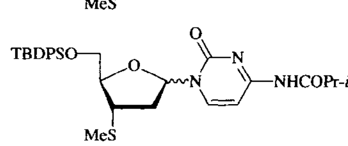
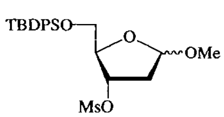
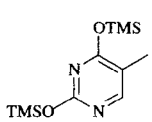
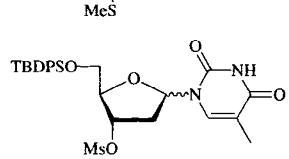
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 2 h 2. NH_3, MeOH, rt, 12 h	 (56)	595
		TMSOTf, MeCN, rt, 20 min	 (66)	1030
		TMSOTf, MeCN, 50°, 3 h	 (78)	835
		TMSOTf, $Cl(CH_2)_2Cl$, 60°, 8 h	 (36)	1031
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 12-16 h	 (78)	1032
		TMSOTf, MeCN, 0°, 3 h; rt, 5 h	 (91)	155, 154
		TMSOTf, MeCN, –20°, 4 h	 (20)	1020
		1. TMSOTf, MeCN, –20°, 4 h 2. NH_3, MeOH	 (42) α:β = 1.4:1	1020
		TMSOTf, MeCN, –20°, 4 h; rt, 17 h	 (28)	1020
		TMSOTf, MeCN, –30°, 15 min; rt, 4 h	 (82) α:β = 1:2	1026

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

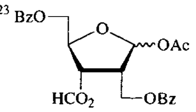
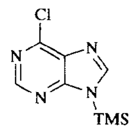
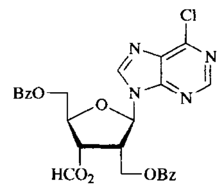
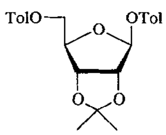
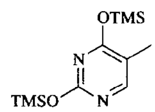
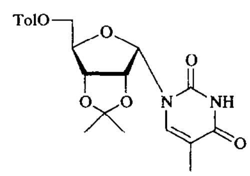
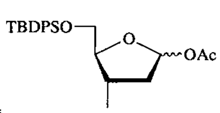
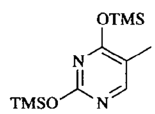
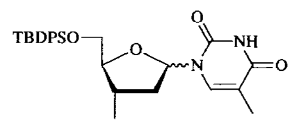
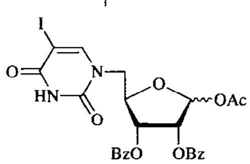
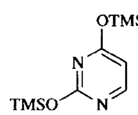
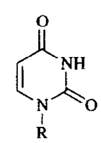
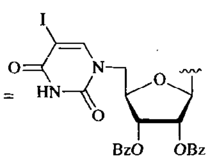
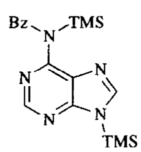
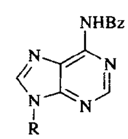
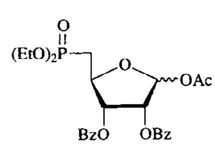
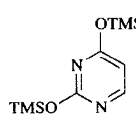
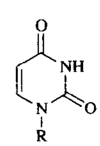
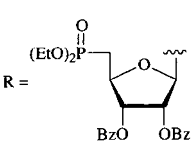
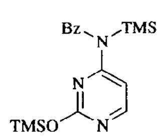
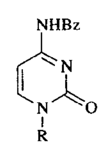
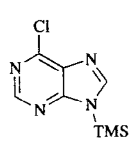
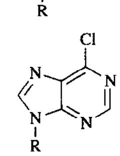
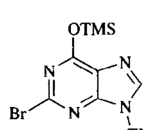
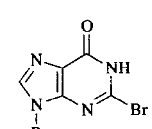
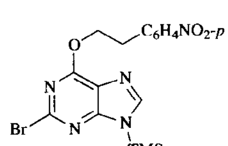
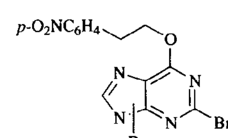
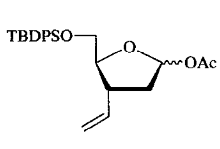
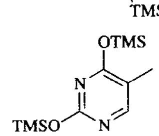
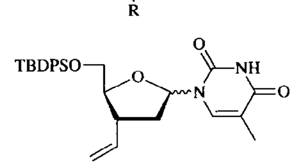
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23} 		TMSOTf, MeCN, rt, 15 min	 (91)	1030
C_{24} 		TMSOTf, $Cl(CH_2)_2Cl$, rt, 2 h	 (65) + β-anomer (10-15)	223
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 12-16 h	 (91) α:β = 1:1.6	1032
C_{25} 		TMSOTf, MeCN	 (89) R = 	1033
		TMSOTf, MeCN	 (56)	1033
		TMSOTf, MeCN, rt, 24 h	 (59) R = 	1034
		TMSOTf, MeCN, rt, 24 h	 (50)	1034
		TMSOTf, MeCN, rt, 24 h	 (60)	1034
		TMSOTf, MeCN, rt, 48 h	 (30)	1034
		TMSOTf, MeCN, rt, 16 h	 (75) N^7:N^9 = 1:19	143
		TMSOTf, $Cl(CH_2)_2Cl$	 (79) α:β = 2:1	297

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

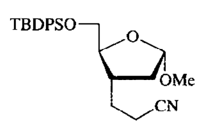
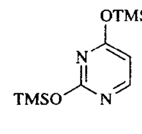
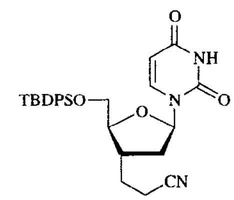
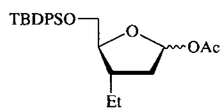
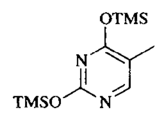
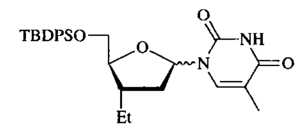
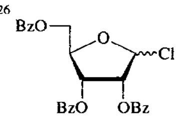
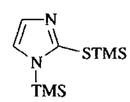
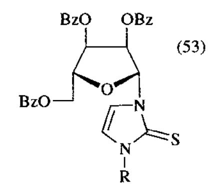
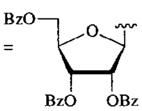
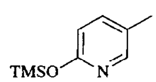
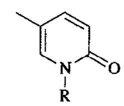
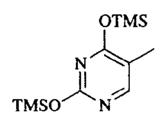
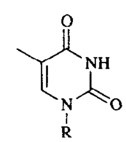
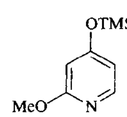
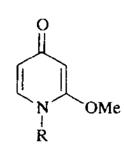
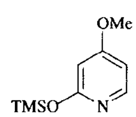
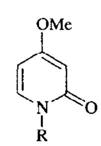
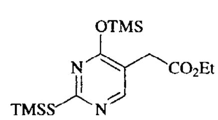
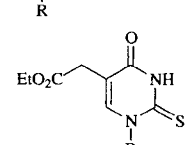
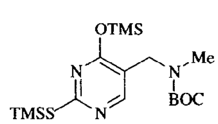
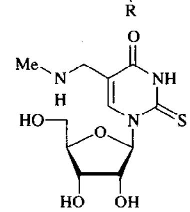
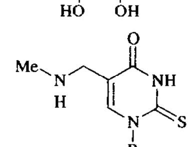
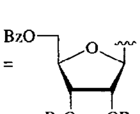
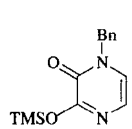
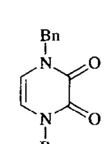
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, MeCN, −30°, 30 min; 20°, 2 h	 (33) + α-anomer (15)	1035
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 12-16 h	 (85) α:β = 1:1.8	1032
C_{26} 		$AgClO_4$, C_6H_6, rt, 24 h	 (53) R = 	701
		AgOTf, CH_2Cl_2, −70°	 (75)	212
		$AgClO_4$, C_6H_6, 20°, 16 h	 (75)	80
		1. AgOTf, $MeNO_2$, −18° 2. MeOH, Amberlite IR 45	 (51)	212a
		1. AgOTf, CH_2Cl_2, −70° 2. MeOH, Amberlite IR 45	 (75)	212
		$AgClO_4$, C_6H_6, rt, 15 min	 (86)	81, 971
		1. $AgClO_4$, PhMe, 24°, 1 h 2. NH_3, MeOH, 24°, 30 h	 (50)	126
		$AgClO_4$, C_6H_6	 (~70) R = 	125
		$AgClO_4$, C_6H_6, rt, 12 h	 (83)	1036

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

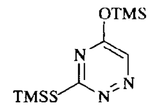
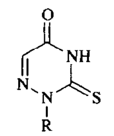
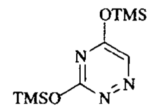
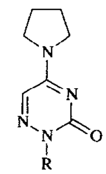
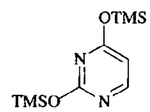
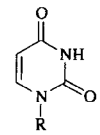
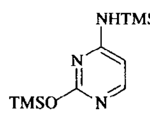
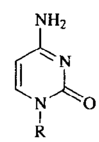
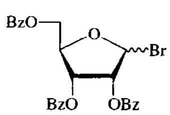
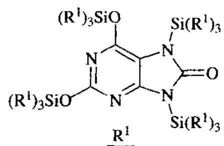
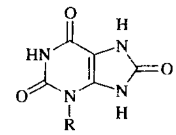
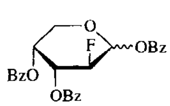
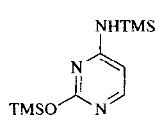
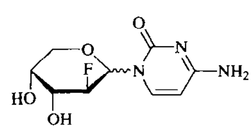
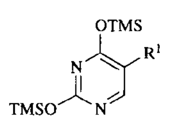
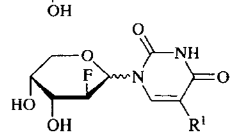
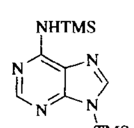
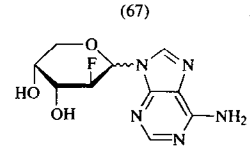
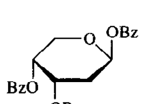
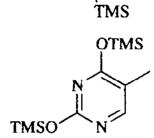
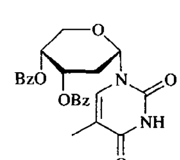
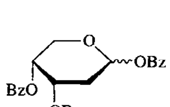
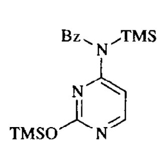
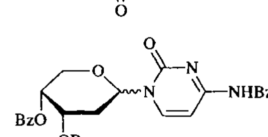
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$AgClO_4$, C_6H_6, rt, 12 h	 (78)	971
		1. $AgClO_4$, C_6H_6, 22°, 1 h 2. pyrrolidine, rt, 23 h	 (46)	79
		AgOTf, $MeNO_2$, −18°	 (62)	212
		AgOTf, $MeNO_2$, −18°	 (50)	212
				
	R^1			
	Me	$AgClO_4$	(90)	73
	Et	$AgClO_4$, PhMe, 50°	(90)	74
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 24 h 2. NH_3, MeOH, 12 h	 (63) α:β = 65:35	1037
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 24 h 2. NH_3, MeOH, 12 h		1037
	R^1		α:β	
	H		(88) 58:42	
	F		(89) 59:41	
	I	step 1 - 60 h	(72) 58:42	
	Me		(85) 59:41	
	Et		(67) 55:45	
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 24 h 2. NH_3, MeOH, 12 h	 (83) α:β = 58:42	1037
		TMSOTf, $Cl(CH_2)_2Cl$	 (63) + β anomer (25)	840
		TMSOTf, $Cl(CH_2)_2Cl$ rt, 4 h	 (94) α:β = 80:20	1037, 1038

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

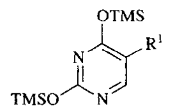
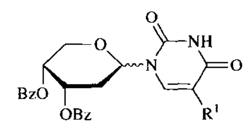
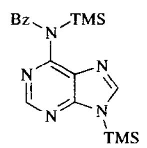
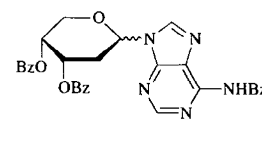
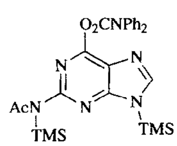
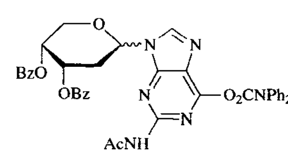
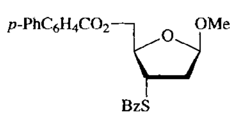
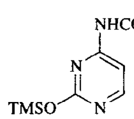
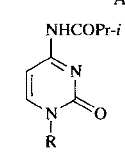
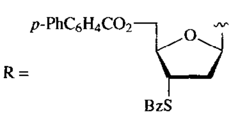
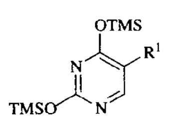
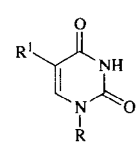
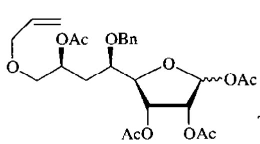
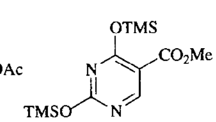
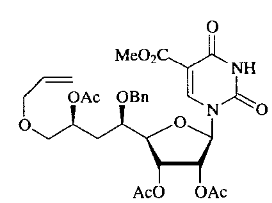
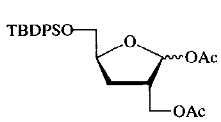
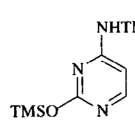
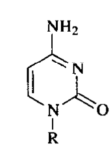
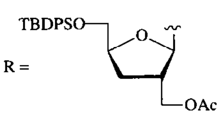
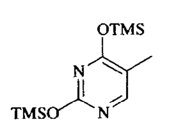
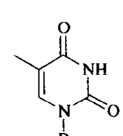
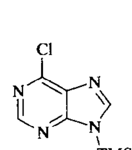
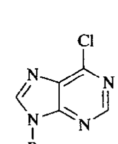
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$ rt, 4 h		1037, 1038
	R^1		$\alpha:\beta$	
	H		(91) 66:34	
	F		(90) 68:32	
	I		(90) 76:24	
	Me		(93) 80:20	
	Et		(93) 73:27	
		$TMSClO_4$, $Cl(CH_2)_2Cl$, reflux 6 h	 (62) $\alpha:\beta = 55:45$	1037
		$TMSClO_4$, $Cl(CH_2)_2Cl$, reflux 6 h	 (55) $\alpha:\beta = 65:35$	1037
		TMSOTf, MeCN, 25°, 5-6 h	 (70) R = 	1020
		TMSOTf, MeCN, 25°, 5-6 h	 R^1: H (64); Me (54)	1020
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 2 h	 (80)	156
		TBDMSOTf, MeCN, CH_2Cl_2, rt, 15 h	 (84) R = 	1039
		TBDMSOTf, MeCN, CH_2Cl_2, rt, 15 h	 I (—)	962
		TBDMSOTf, MeCN, CH_2Cl_2, 0°, 30 min rt. 15 h	I (97)	1039
		TBDMSOTf, MeCN, CH_2Cl_2, 0°, 30 min rt. 15 h	 (87)	1039

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

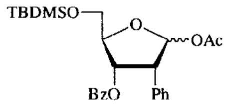
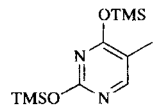
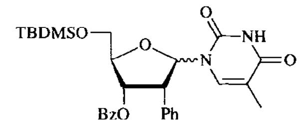
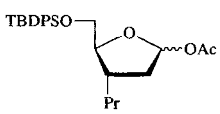
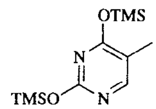
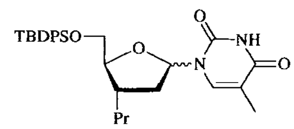
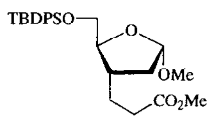
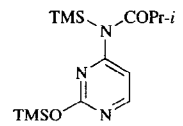
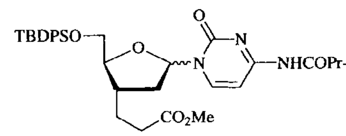
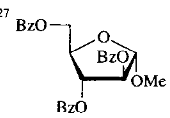
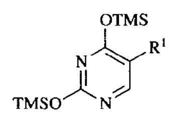
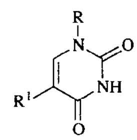
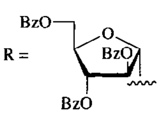
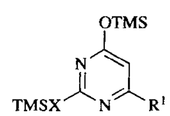
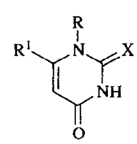
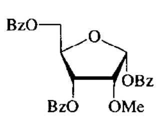
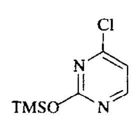
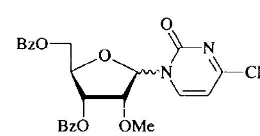
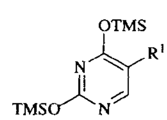
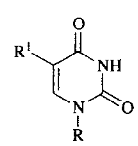
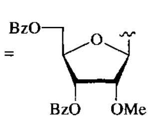
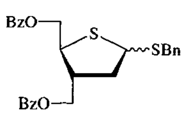
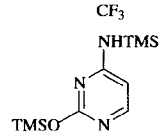
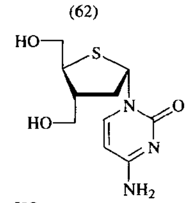
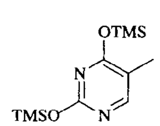
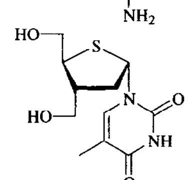
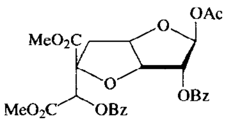
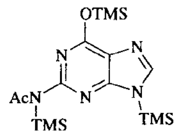
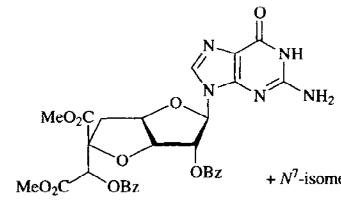
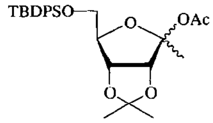
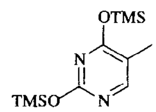
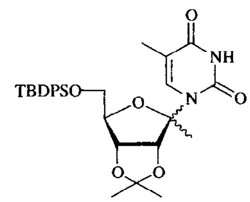
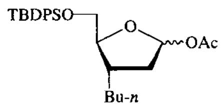
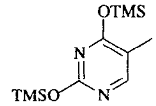
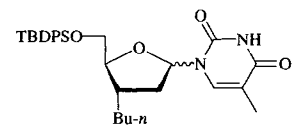
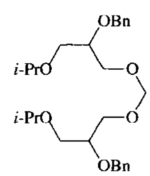
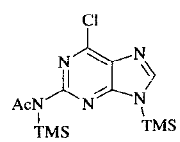
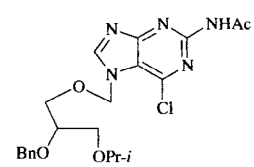
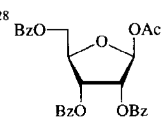
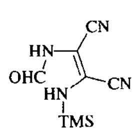
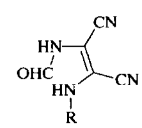
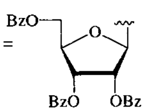
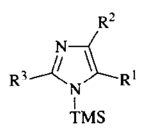
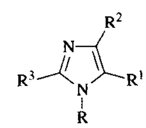
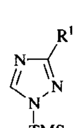
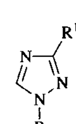
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$, rt	 (68) α:β = 1:3.5	829
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 12-16 h	 (88) α:β = 1:1.7	1032
		TMSOTf, MeCN, −35°, 1.5 h	 (59)	1035
C_{27} 		TMSOTf, MeCN, rt, 5 d	 R = 	370
	R^1			
	Cl		(81)	
	Me		(63)	
	n-C_6H_{13}		(6)	
	N-4-benzylpiperidinyl		(68)	
		TMSOTf, MeCN, rt, 5 d		366
	X R^1		bis(riboside)	
	O Me		(2) (81)	
	O Et		(38) (46)	
	S Me		(24) (—) N^3 products	
	S Et		(66) (—)	
		TMSOTf, MeCN, rt, 30 min	 (96) α:β = 1:14	538a
		TMSOTf, MeCN, rt, 30 min	 R = 	538a
	R^1			
	H		(75)	
	F		(68)	
	NO_2		(56)	
	Me		(55)	
	CF_3		(62)	
		1. TMSOTf, MeCN, −20°, 1 h 2. NH_3, MeOH	 (36) + β-anomer (28)	1016
		1. TMSOTf, $Hg(OAc)_2$, CH_2Cl_2, rt, 24 h 2. NH_3, MeOH	 (35) + β-anomer (24)	1016

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 4 d	 (22) + N^7-isomer (41)	782
		TMSOTf, MeCN, 0°, 1 h	 α:β; 0° (66) 1.2:1; –30° (45) 1:2	1040
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 12-16 h	 (86) α:β = 1:1.7	1032
		TMSOTf, $Cl(CH_2)_2Cl$, –30°, 2 h	 (51)	521
C_{28} 		TMSOTf, CH_2Cl_2, rt, 2.5 h	 (60) R = 	161
		TMSOTf		

R^1	R^2	R^3	Conditions	Product	N^7-isomer	Refs.
NO_2	$SCH_2P(O)(OEt)_2$	H	MeCN, rt, 42 min	(19)	(7)	1041
NO_2	SMe	H	MeCN, 0°, 3 min	(80)	(—)	1041
SMe	NO_2	H	$Cl(CH_2)_2Cl$, rt, 16 h	(51)	(—)	1041
NO_2	SCH_2CO_2Me	H	MeCN, 0°, 90 s	(72)	(0.8)	1041
NO_2	$SCH_2CH(CO_2Me)CH_2CO_2Me$	H	MeCN, 0°, 90 s	(63)	(—)	1041
CO_2Me	CO_2Me	Me	$Cl(CH_2)_2Cl$, rt, 3 h	(60)	(—)	502
CO_2Me	CO_2Me	Me	$Cl(CH_2)_2Cl$, rt, 18 h	(60)	(—)	1042
CO_2Me	CO_2Me	Et	$Cl(CH_2)_2Cl$, rt, 3 h	(52)	(—)	502
CO_2Me	CO_2Me	*i*-Pr	$Cl(CH_2)_2Cl$, rt, 3 h	(83)	(—)	502
CO_2Me	CO_2Me	Bu	$Cl(CH_2)_2Cl$, rt, 3 h	(55)	(—)	502
CO_2Et	CO_2Et	Ph	$Cl(CH_2)_2Cl$, rt, 3 h	(45)	(—)	502
CO_2Et	CO_2Et	Bn	$Cl(CH_2)_2Cl$, rt, 3 h	(61)	(—)	502

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf		

R^1	Conditions	Product(s) and Yield(s) (%)	Refs.
H	$Cl(CH_2)_2Cl$, MeCN, 24°, 3 h	(61)	133
CO_2Me	$Cl(CH_2)_2Cl$, MeCN, 4°, 4 h	(47) + N^2-isomer (20)	133
CH_2CO_2H	$Cl(CH_2)_2Cl$, C_6H_6, 100°, 4 h	(86)	1043

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

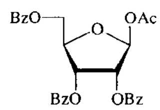
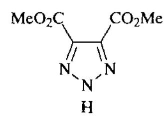
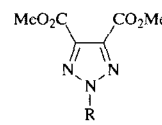
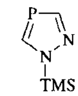
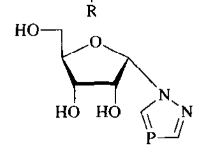
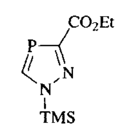
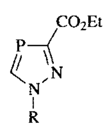
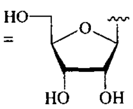
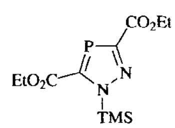
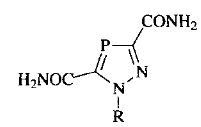
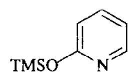
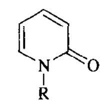
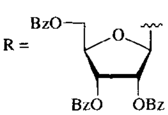
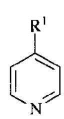
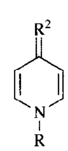
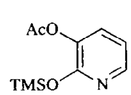
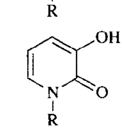
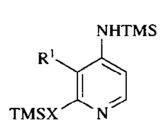
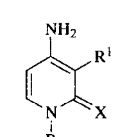
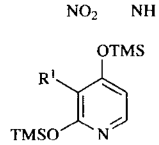
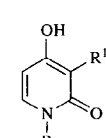
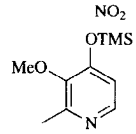
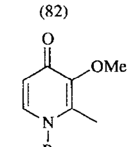
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		HMDS, TMSOTf, MeCN, rt, 12 h	 (94)	1044
		1. TMSOTf, MeCN, rt, 8 h 2. NH_3, MeOH	 (16)	214
		1. TMSOTf, MeCN, rt, 16 h 2. NH_3, MeOH	 (44) R = 	214
		1. TMSOTf, MeCN, rt, 24 h 2. NH_3, MeOH	 (—)	214
		TMSOTf, $Cl(CH_2)_2Cl$	 R = 	
		82°, 2 h	(86)	132
		C_6H_6, 100°, 1.5 h	(85)	1043
		reflux, 1.5 h	(86)	133
		TMSOTf, $Cl(CH_2)_2Cl$, reflux,		
			R^1 OTMS, R^2 O, 3.5 h (83)	133
			R^1 NHTMS, R^2 NH, 2.5 h (80)	133
		TMSOTf, CH_2Cl_2, rt, 24 h	 (81)	1045
		TMSOTf, $Cl(CH_2)_2Cl$, rt		
	R^1 = Cl, X = O	24 h	(99)	861 1046
	R^1 = Br, X = O	18 h	(41)	1046
	R^1 = NO_2, X = NH	—	(—)	1047
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 18 h		1046
	R^1 = Cl		(56)	
	R^1 = Br		(84)	
	R^1 = NO_2		(82)	
		TMSOTf, CH_2Cl_2, rt, 24 h	 (88)	1045

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

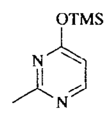
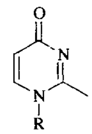
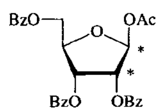
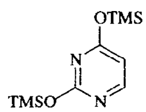
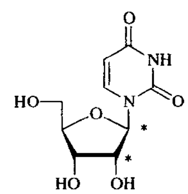
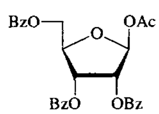
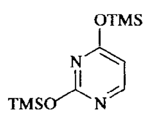
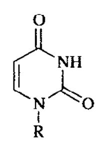
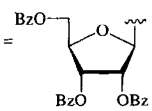
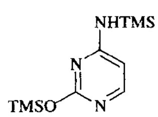
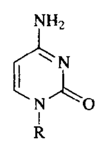
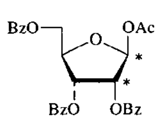
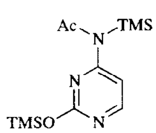
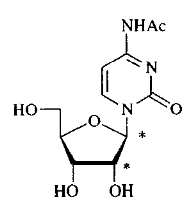
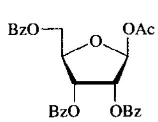
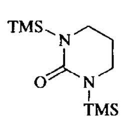
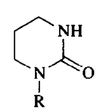
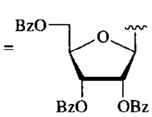
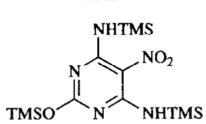
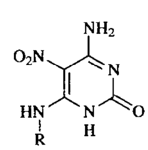
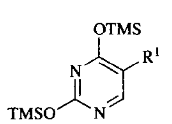
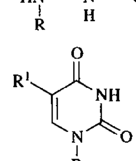
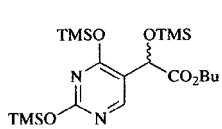
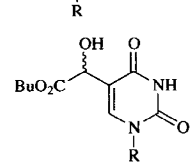
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 2 h	 (98)	845
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 4 h 2. NH_3, MeOH	 (89) * ^{13}C-enriched	36
		$TMSClO_4$, $Cl(CH_2)_2Cl$	 (56) R = 	
		22°, 7 d	(76)	132
		82°, 6 h	(80)	132
		24°, 1 week	(81)	133
		C_6H_6, 100°, 4 h	(80)	1043
		C_6H_6, 24°, 1 week	(76)	1043
		TMSOTf, $Cl(CH_2)_2Cl$, C_6H_6, 100°, 1 h	 I (85)	1043
		TMSOTf, $Cl(CH_2)_2Cl$		
		reflux, 1 h	I (98)	133
		82°, 1 h	I (90)	132
		20°, 1 h	I (90)	1043
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 2 h 2. NH_3, MeOH, 16 h	 (95) * ^{13}C-enriched	36
		TMSOTf, $Cl(CH_2)_2Cl$, 60°, 1 h	 (16) R = 	162
		TMSOTf, MeCN, rt, 18 h	 (72)	455
		TMSOTf, $Cl(CH_2)_2Cl$, 24°, time	 R^1 / time: NO_2, 2 h (93); OMe, 4-7 h (86-90)	133 193, 133
		TMSOTf	 (76) α:β = 1:1	611

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

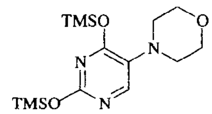
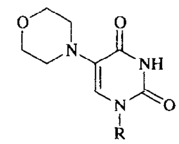
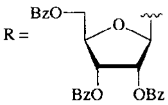
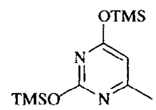
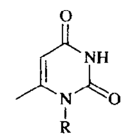
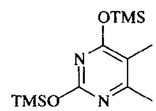
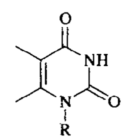
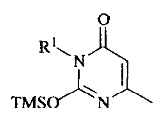
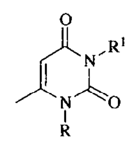
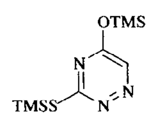
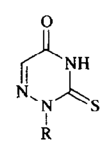
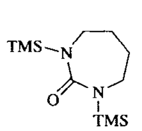
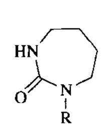
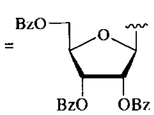
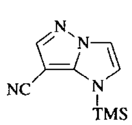
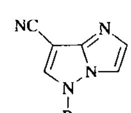
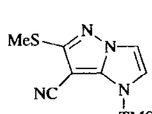
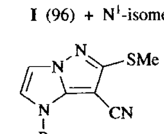
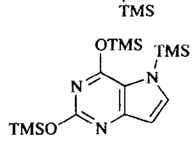
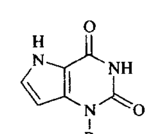
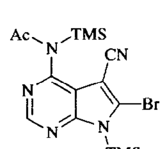
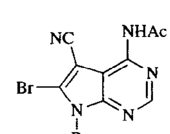
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$, 24°, 10 or 24 h	 (95-99) R = 	133, 193
		TMSOTf, $Cl(CH_2)_2Cl$, 24°	 **I** (47) + N^3-isomer (18) + N^1,N^3-bis(riboside) (12)	193
		TMSOTf, MeCN, 24°	**I** (71) + N^3-isomer (2) + N^1,N^3-bis(riboside) (11)	193
		TMSOTf, $Cl(CH_2)_2Cl$, MeCN, 4 to 24°, 2 h	**I** (75) + N^3-isomer (4) + N^1,N^3-bis(riboside) (11)	133
		TMSOTf, $Cl(CH_2)_2Cl$, 24°, 3 h	 (82) + N^3-isomer (9)	133, 193
		TMSOTf, MeCN	 R^1: Me (—); Bn (85)	256
		$TMSClO_4$, $Cl(CH_2)_2Cl$, 82°, 3 h	 (67)	132
		TMSOTf, $Cl(CH_2)_2Cl$, 25°, 18 h	 **I** (14) R = 	162
		TMSOTf, $Cl(CH_2)_2Cl$, 60°, 1 h	**I** (10)	162
		TMSOTf, C_6H_6, 25°, 18 h	**I** (7)	162
		TMSOTf, MeCN	 **I**	
		0-rt, 6 d	**I** (53) + N^1-isomer (47)	1049
		0-5°, 1 h	**I** (96) + N^1-isomer (4)	1049
		TMSOTf, MeCN, 0-5°, 2 d	 (89)	1049
		TMSOTf, MeCN, rt, 12 h	 (82)	362
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 1 h; 80-85°, 20 h	 (90)	1050

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

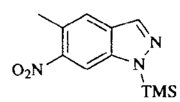
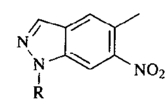
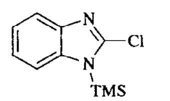
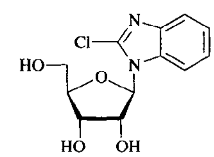
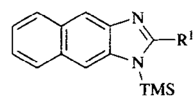
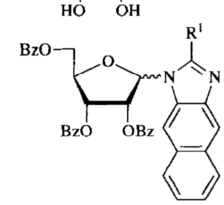
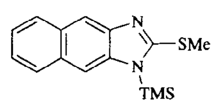
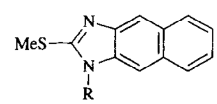
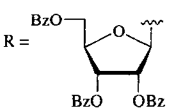
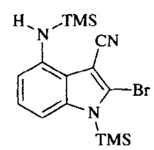
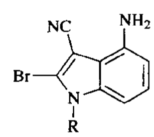
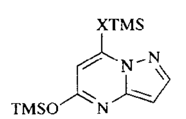
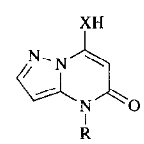
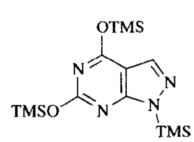
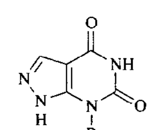
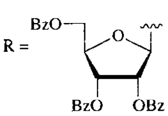
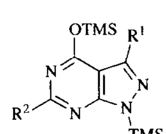
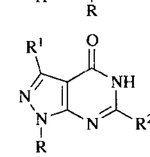
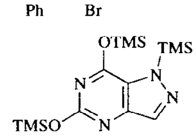
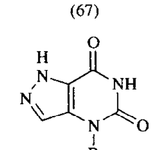
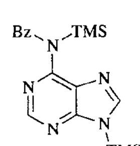
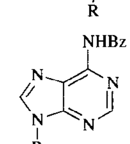
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 6 h	 (64)	1051
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1 h 2. NaOH, EtOH	 (81)	1052
		TMSOTf	 R^1: CF_3 (—); CN (—)	1053 1053
		TMSOTf, $Cl(CH_2)_2Cl$, 25°, 24 h	 (76) R = 	1054
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 1 h; 75-80°, 18 h; reflux, 3 h	 (88)	1050
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 6 h	 X: NH (78); O (55)	361 361
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 6 h	 (66) R = 	361
		TMSOTf, MeCN		
	R^1 Br, R^2 H	reflux, 1 week	(29)	1055
	R^1 CN, R^2 H	−20° to rt, 4 h	(46)	1055
	R^1 Ph, R^2 Br	rt, 16 h	(67)	1056
		TMSOTf, MeCN, rt, 12 h	 (56)	362
		TMSOTf, $Cl(CH_2)_2Cl$, PhMe, rt, 1 h	 (92)	1048

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

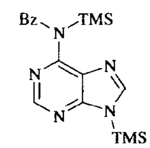
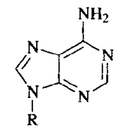
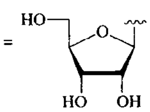
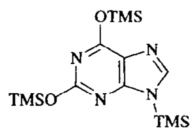
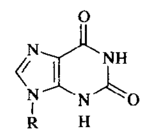
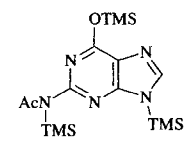
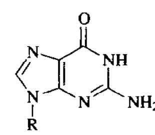
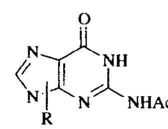
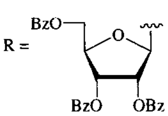
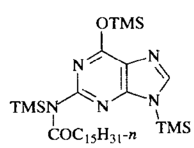
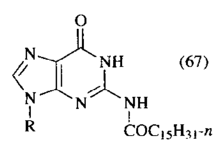
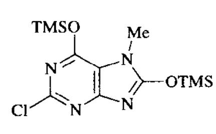
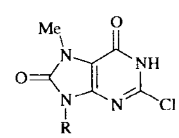
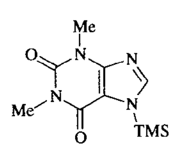
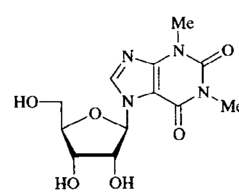
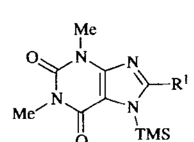
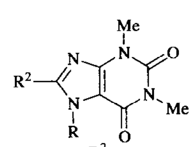
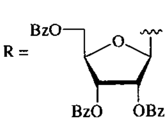
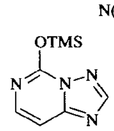
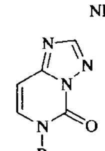
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $TMSClO_4$, $Cl(CH_2)_2Cl$, 82°, 7 h 2. NH_3, MeOH	 **I** (81) R = 	132
		1. $TMSClO_4$, $Cl(CH_2)_2Cl$, 82°, 7 h 2. NH_3, MeOH	**I** (81)	133
		1. $TMSClO_4$, $Cl(CH_2)_2Cl$, C_6H_6, 22°, 16 h 2. NH_3, MeOH	**I** (86)	1043
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1 h 2. NH_3, MeOH	 (49)	133
		1. TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1.5 h 2. NH_3, MeOH	 (66)	133
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1.5 h	 (79) N^7:N^9 = 1:6 R = 	142
		TMSOTf, $Cl(CH_2)_2Cl$, PhMe, rt, 4 h	 (67) + N^7-β-isomer (10)	1048
		TMSOTf, MeCN, reflux, 12 h	 (85)	1057
		1. TMSOTf, $Cl(CH_2)_2Cl$, 24°, 1 h 2. NH_3, MeOH	 (82)	133
		TMSOTf, $Cl(CH_2)_2Cl$, rt	 R = 	1058
	R^1		R^2	
	Cl	10 h	Cl (72)	
	N(Bn)TMS	6 h	NHBn (61)	
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 3.5 h	 (82)	957

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

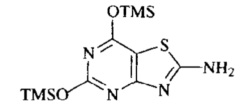
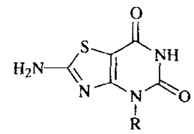
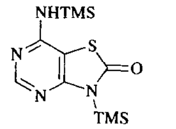
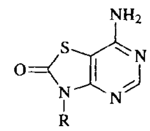
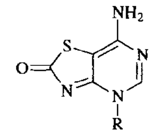
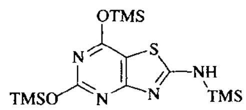
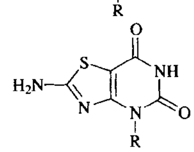
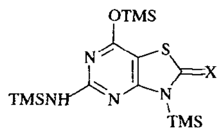
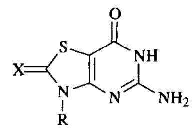
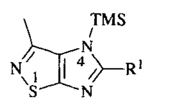
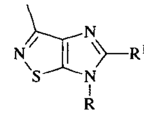
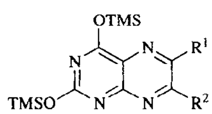
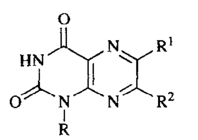
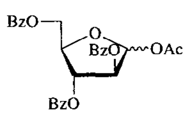
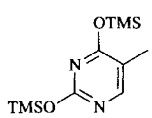
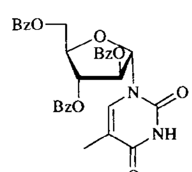
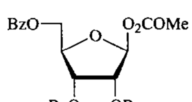
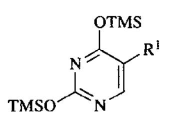
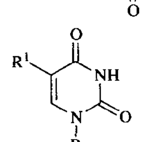
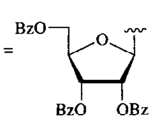
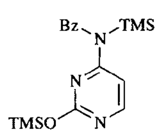
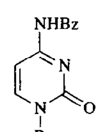
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, MeCN, rt, 12 h	 (25)	361, 1058
		TMSOTf, MeCN, rt, 12 h; reflux, 2 d	 (24)	1058
		TMSOTf, MeCN, rt, 12 h	 (95)	1058
		TMSOTf, MeCN, rt, 12 h	 (82)	361
		TMSOTf, MeCN, rt, 16 h	 X: O (77); S (59)	1058
		TMSOTf, MeCN, 80°, 0.5-1.5 h	 R^1: H (37) + N^4-isomer (26); SMe (61)	350
		TMSOTf, $Cl(CH_2)_2Cl$		
	R^1 / R^2			
	H / H	24°, 1.3 h	(93)	133
	H / H	100°, 4 h	(84)	1043
	H / H	24°, 24 h	(64)	132
	p-ClC_6H_4 / H	rt, 3 h	(84)	1059
	H / p-ClC_6H_4	rt, 3 h	(71)	1059
	p-BrC_6H_4 / H	rt, 2 h	(90)	1060
	H / p-BrC_6H_4	rt, 2 h	(84)	1060
		TMSOTf, MeCN, rt, 18 h	 (44)	365
		AgOTf, $Ph_2Sn{=}S$, MeCN	 R = 	124
	R^1: H	80°, 2 h	(99)	
	R^1: Me	60°, 5 h	(96)	
		AgOTf, $Ph_2Sn{=}S$, MeCN, 60°, 4.5 h	 (57)	124

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

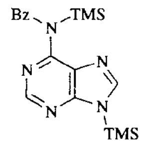
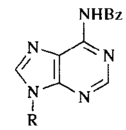
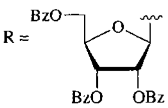
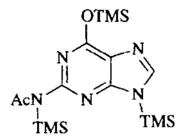
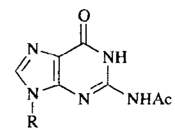
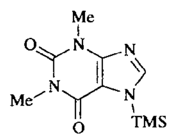
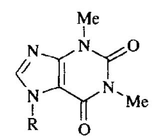
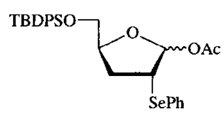
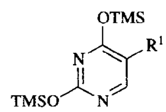
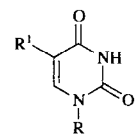
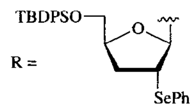
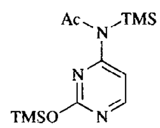
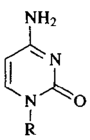
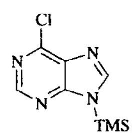
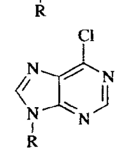
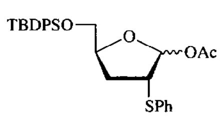
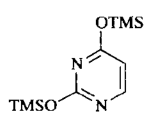
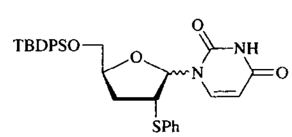
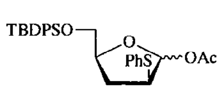
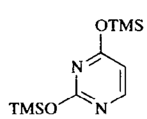
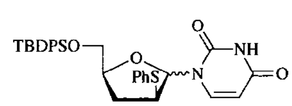
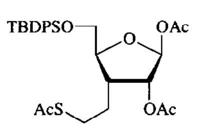
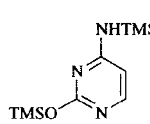
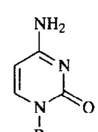
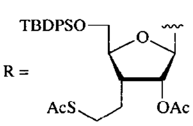
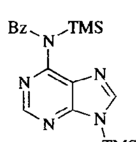
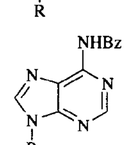
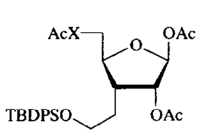
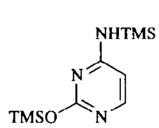
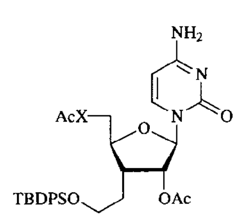
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		AgOTf, Ph_2Sn=S, MeCN, reflux, 14 h	 (49) R = 	124
		AgOTf, Ph_2Sn=S, MeCN, reflux, 16h	 (77)	124
		AgOTf, Ph_2Sn=S, MeCN, 60°, 1.5 h	 (96)	124
C_{29} 		TMSOTf, $Cl(CH_2)_2Cl$, 5 to 24°, 15 min	 R^1: H (67); Me (78) R = 	230a
		TMSOTf	 (72)	230a
		TMSOTf	 (89)	230a
		TMSOTf, $Cl(CH_2)_2Cl$, rt	 I (90) α:β = 21:79	229, 228
		TMSOTf, MeCN, rt, 12 h	I (96) α:β = 11:89	229, 228
		TMSOTf, $Cl(CH_2)_2Cl$,	 (—) α:β = 20:80	229
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 2.5 h	 (86) R = 	932
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 15 h	 (90)	932
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 30 min	 X: O (90); S (78)	1061

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

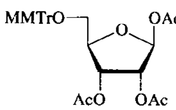
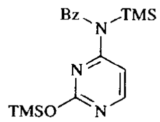
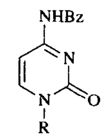
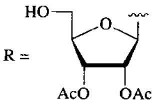
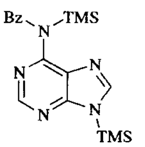
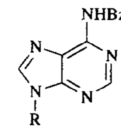
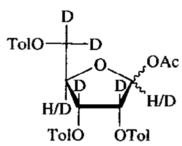
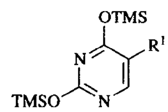
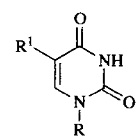
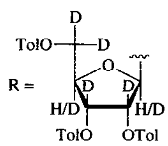
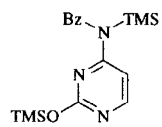
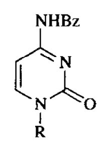
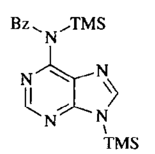
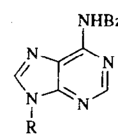
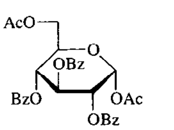
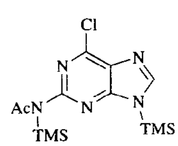
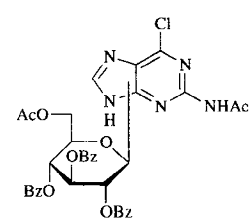
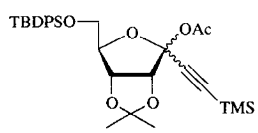
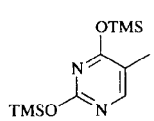
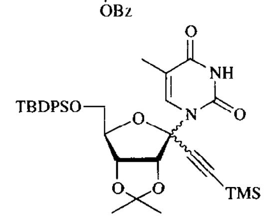
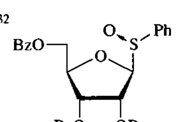
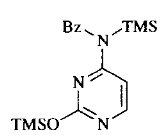
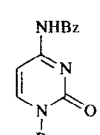
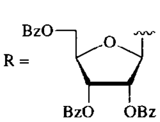
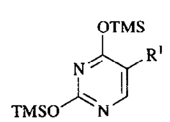
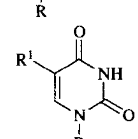
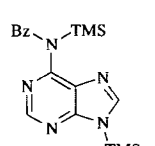
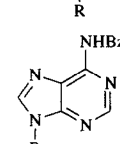
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{30} 		TMSOTf, $Cl(CH_2)_2Cl$, 20°, 16 h	 (70) R = 	931
		TMSOTf, $Cl(CH_2)_2Cl$, 20°, 16 h	 (66)	931
C_{31} 		TMSOTf, $Cl(CH_2)_2Cl$, 70°, 4 h	 R^1: H (75), Me (91); R = 	1062
		TMSOTf, $Cl(CH_2)_2Cl$, 70°, 4 h	 (85)	1062
		TMSOTf, $Cl(CH_2)_2Cl$, 70°, 4 h	 (60)	1062
		TMSOTf, $Cl(CH_2)_2Cl$, 135°, 16 h	 (69) N^9:N^7 = 98:2	409
		TMSOTf, MeCN, 0°, 4 h	 (97)	1040
C_{32} 		TMSOTf, $Cl(CH_2)_2Cl$, rt, 1 min	 (95) R = 	412
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 1 min	 R^1: H (90), Me (92)	412
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 1 min	 I (40)	412
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 0.5 h	I (90)	412

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

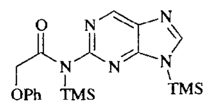
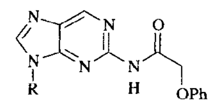
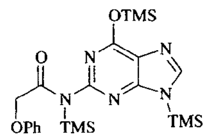
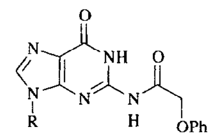
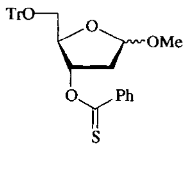
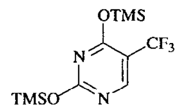
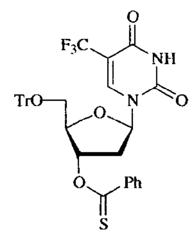
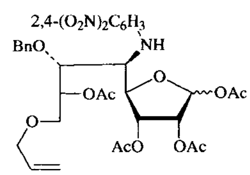
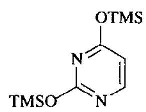
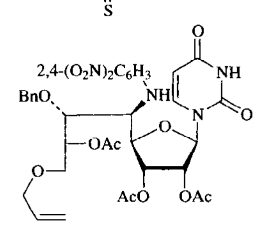
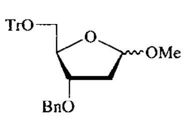
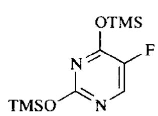
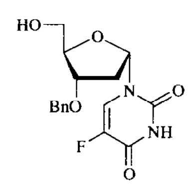
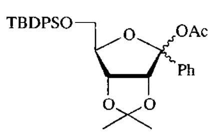
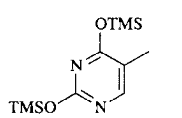
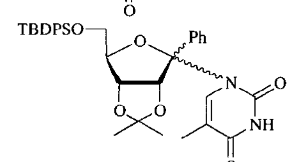
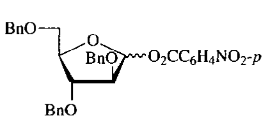
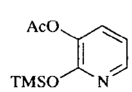
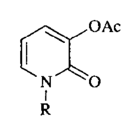
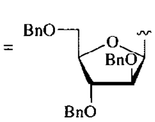
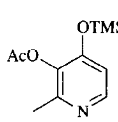
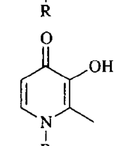
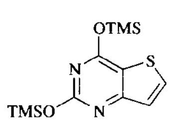
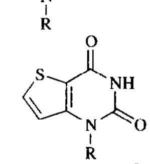
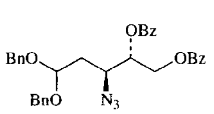
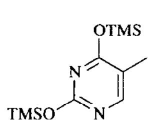
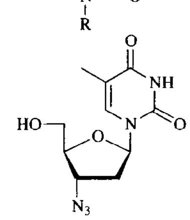
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 0.5 h	 (60)	412
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 0.5 h	 (65) + N^7-isomer (22)	412
		TMSOTf, MeCN, −40 to −45°, 0.5 h	 (89)	1063
		TMSOTf, MeCN, reflux, 45 min	 (92)	157
		TMSOTf, CH_2Cl_2, < 5°, 2.5 h	 (31) + β-anomer (22)	913
		TMSOTf, MeCN, 0°, 3.5 h	 (27)	1040
C_{33} 		TMSOTf, CH_2Cl_2, rt, 24 h	 (51) + α-anomer (27) R = 	1045
		1. TMSOTf, CH_2Cl_2, rt, 24 h 2. MeCOCl, Et_3N	 (86) α:β = 1:2	1045
		TMSOTf, MeCN, rt, 24 h	 (12)	893
		1. TMSOTf, $Cl(CH_2)_2Cl$ 2. NaOH, MeOH 3. H_2SO_4, MeOH	 (67)	299

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

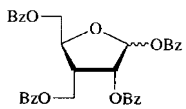
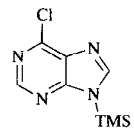
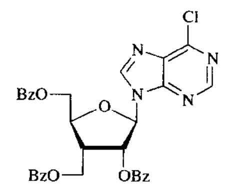
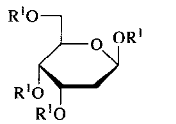
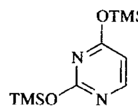
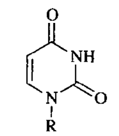
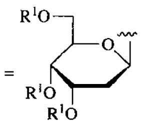
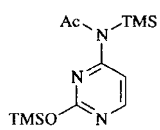
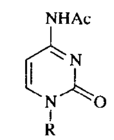
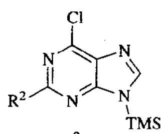
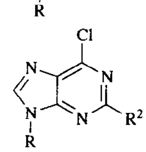
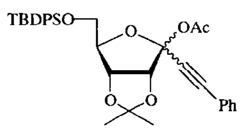
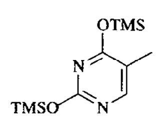
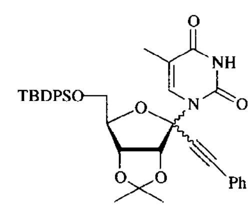
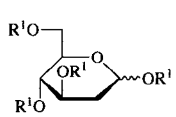
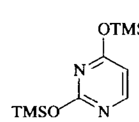
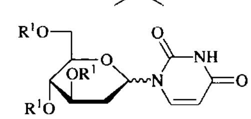
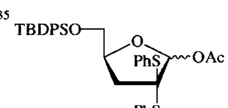
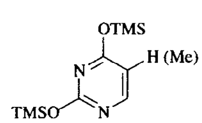
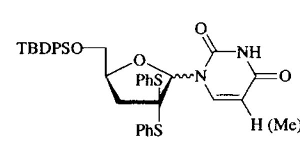
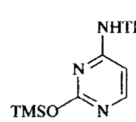
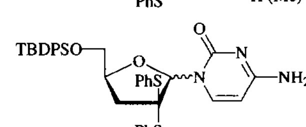
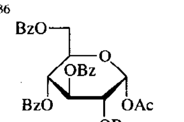
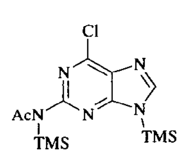
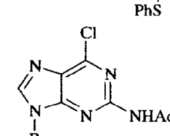
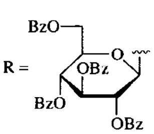
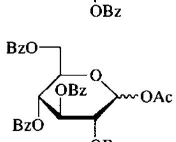
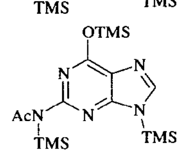
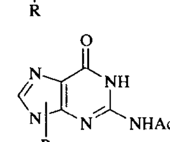
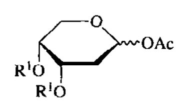
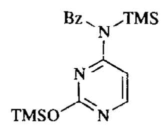
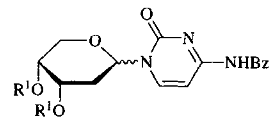
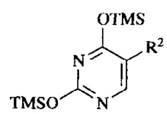
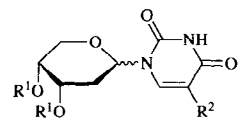
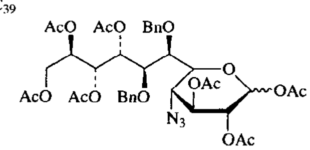
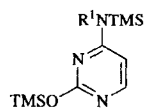
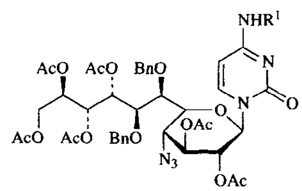
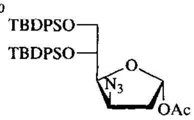
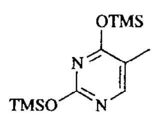
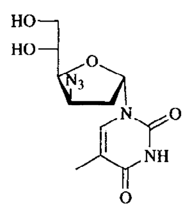
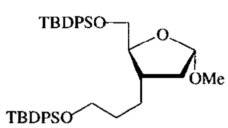
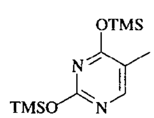
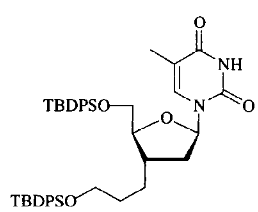
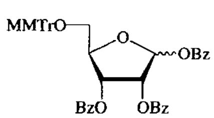
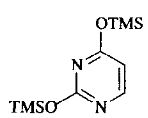
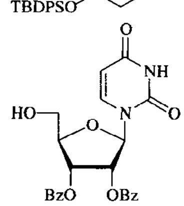
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{34}				
		TMSOTf, MeCN, 80°, 1 h	 (78)	1064
 $R^1 = p\text{-}O_2NC_6H_4CO_2$		1. TMSOTf, MeCN, reflux, 2 h 2. Na_2CO_3	 (75) R = 	1065
		1. TMSOTf, MeCN, 25°, 10 d 2. Na_2CO_3	 (82)	1065
		TMSOTf, MeCN		1065
	R^2			
	H	25°, 12 h, $NaHCO_3$	(58) + N^7-β-isomer (30)	
	Cl	rt, 16 h	(66) + α-anomer (8)	
		TMSOTf, MeCN, 0°, 4.5 h	 (94) α:β = 1:2.4	1040
 $R^1 = p\text{-}O_2NC_6H_4CO_2$		TMSOTf, $Cl(CH_2)_2Cl$	 (—) α:β = 3:2	1038
C_{35}				
		TMSOTf, MeCN, 0°, 4 h	 (83) α:β = 19:81	305a, 305
		TMSOTf, MeCN, 0°, 4 h	 (79) α:β = 20:80	305a
C_{36}				
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 1 h	 (70) + N^7-isomer (2) R = 	409
		TMSOTf, $Cl(CH_2)_2Cl$, reflux, 16 h	 (56) N^7:N^9 = 1:8	142

TABLE IV. REACTIONS WITH TRIMETHYLSILYL AND SILVER TRIFLATES AND PERCHLORATES (*Continued*)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{38}  $R^1 = p\text{-}t\text{-}BuC_6H_4CO_2$		TMSOTf, $Cl(CH_2)_2Cl$, rt, 4 h	 (95)	1037
		TMSOTf, $Cl(CH_2)_2Cl$, rt, 4 h	 R^2 / F (94) 58:42 / I (93) 63:37 / Me (94) 75:25 (α:β)	1037
C_{39} 		TMSOTf, $PhNO_2$, 127°, 3.5 h	 R^1 / H (76) / Ac (76)	160 / 159
C_{40} 		1. TMSOTf, MeCN, −20°, 90 min 2. Bu_4NF, THF, rt, 24 h	 (31) + β-anomer (24)	980, 961
		TMSOTf, MeCN, −10°, 1 h; rt, 12 h	 (42) + α-anomer (38)	1066
		TMSOTf, $Cl(CH_2)_2Cl$, 20°, 16 h	 (70)	931

[a] The 1-β-methoxy sugar does not react under these conditions.

TABLE V. REACTIONS WITH TITANIUM TETRACHLORIDE AS CATALYST

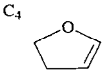
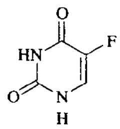
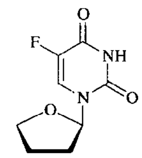
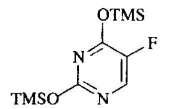
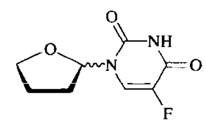
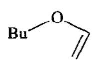
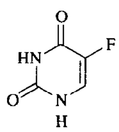
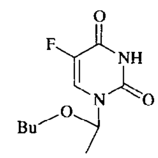
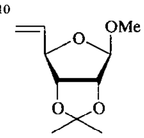
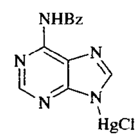
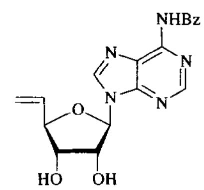
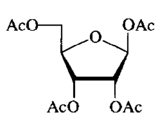
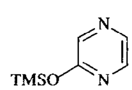
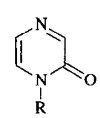
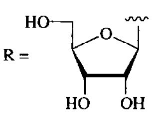
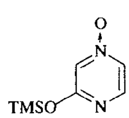
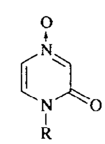
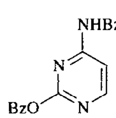
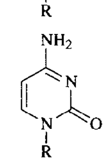
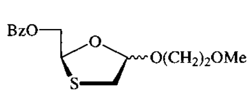
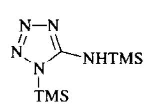
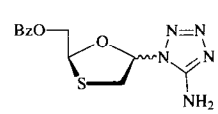
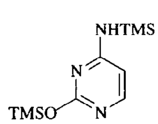
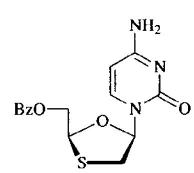
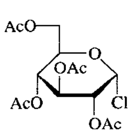
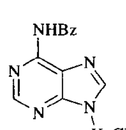
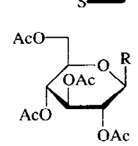
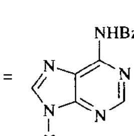
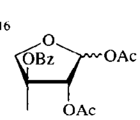
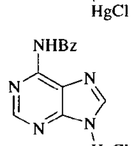
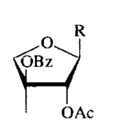
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		$TiCl_4$, Py, 80°, 4 h	 (69)	1067
C_6 		$TiCl_4$, CH_2Cl_2, rt, 0.5 h	 (60)	528
		$TiCl_4$, Py, reflux, 2 h	 (49) + N^1,N^3-bis(isomer) (17)	638
C_{10} 		1. $TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 22 h 2. NaOMe, MeOH	 (44)	1068
C_{13} 		1. $TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 5 h 2. NaOMe, MeOH	 (40) R = 	1069
		1. $TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 4 h 2. NaOMe, MeOH	 (10)	1069
		1. $TiCl_4$, $Cl(CH_2)_2Cl$, rt, 15 h 2. NH_3, MeOH	 (82)	424
C_{14} 		$TiCl_4$, MeCN, 0°, 2 h; rt, 24 h	 (30) *cis:trans* = 1:1	970
		$TiCl_4$, $Cl(CH_2)_2Cl$, rt, 12 h	 (56)	1070
		$TiCl_4$, xylene, reflux, 5 h	 (27) R = 	1071
C_{16} 		$TiCl_4$	 (56)	1072

TABLE V. REACTIONS WITH TITANIUM TETRACHLORIDE AS CATALYST (*Continued*)

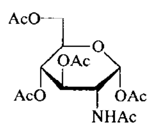
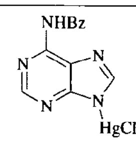
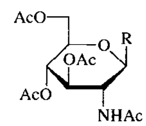
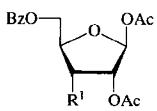
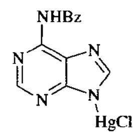
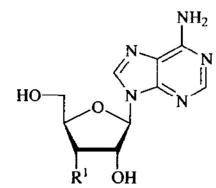
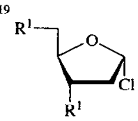
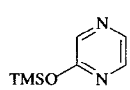
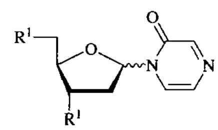
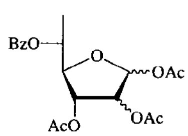
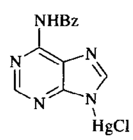
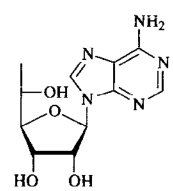
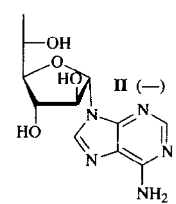
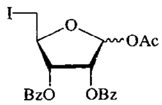
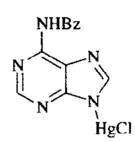
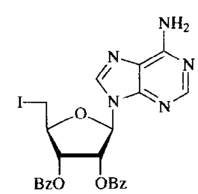
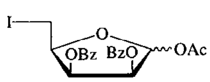
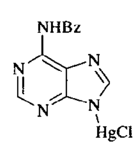
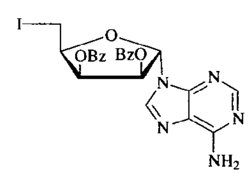
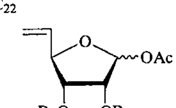
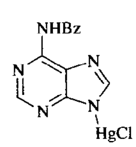
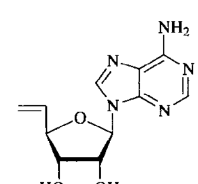
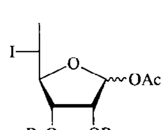
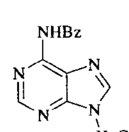
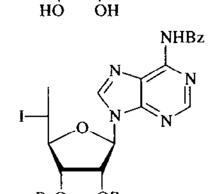
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$TiCl_4$, $CdCO_3$, xylene, reflux, 1.5 h	 (30)	1071
C_{17-20} 		1. $TiCl_4$, $Cl(CH_2)_2Cl$, Celite, reflux, 24 h 2. NaOMe, MeOH	 R^1: Me (63); Et (46); Bu-*n* (58)	1072a
C_{19}  $R^1 = p\text{-}ClC_6H_4CO_2$		$TiCl_4$, $Cl(CH_2)_2Cl$, MS, rt, 24 h	 (86) $\alpha:\beta = 2.1:1$	1073
		1. $TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 21 h 2. NaOMe, MeOH	 I +  II (—) 1:1	1074
		1. $TiCl_4$, $Cl(CH_2)_2Cl$, Celite 545, reflux, 21 h 2. NaOMe, MeOH	II (—)	1074
C_{21} 		$TiCl_4$, $Cl(CH_2)_2Cl$, Celite 545, reflux, 24 h	 (—)	1075
		$TiCl_4$, $Cl(CH_2)_2Cl$, Celite 545, reflux, 21 h	 (—)	1075
C_{22} 		1. $TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 22 h 2. NaOMe, MeOH	 (44)	1068
		$TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 23 h	 (—)	1076

TABLE V. REACTIONS WITH TITANIUM TETRACHLORIDE AS CATALYST (*Continued*)

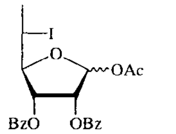
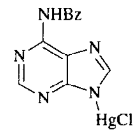
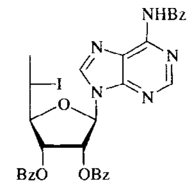
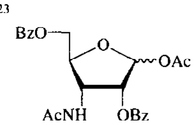
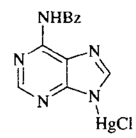
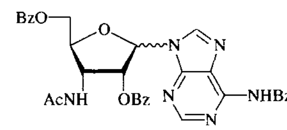
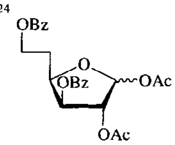
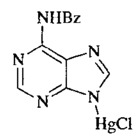
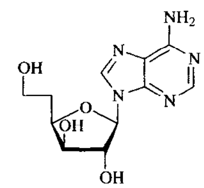
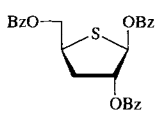
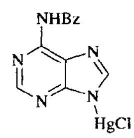
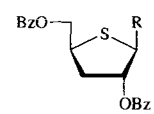
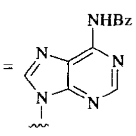
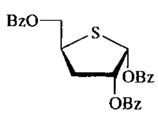
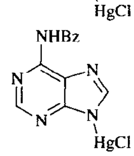
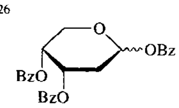
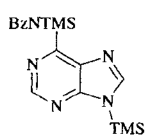
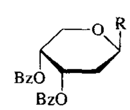
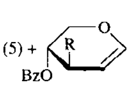
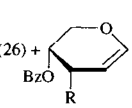
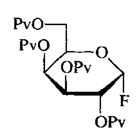
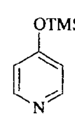
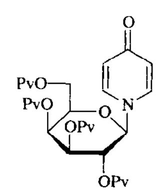
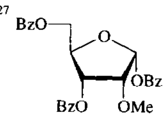
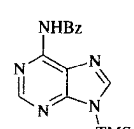
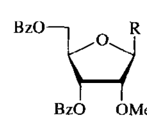
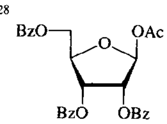
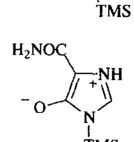
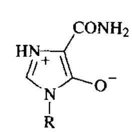
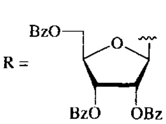
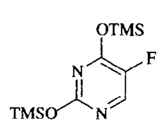
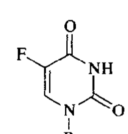
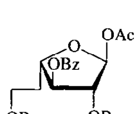
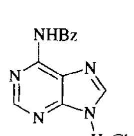
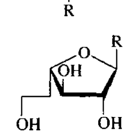
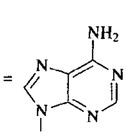
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 23 h	 (—)	1076
C_{23} 		$TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 19 h	 (57)	85
C_{24} 		1. $TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 7 h 2. NaOMe, MeOH	 (30)	1077
		$TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 7 h	 **I** (78) R = 	1078
		$TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 7 h	**I** (82)	1078
C_{26} 		$TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 4 h	 (5) +  (26) +  (24)	841
		$TiCl_4$, $Cl(CH_2)_2Cl$, 70°	 (100)	1019a
C_{27} 		$TiCl_4$	 (70)	846
C_{28} 		$TiCl_4$, $MeNO_2$	 (52) R = 	241
		$TiCl_4$, $Cl(CH_2)_2Cl$ or MeCN, rt, 3 h	 (39-68)	514b
C_{29} 		1. $TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 12 h 2. NaOMe, MeOH	 (28) R = 	1077

TABLE V. REACTIONS WITH TITANIUM TETRACHLORIDE AS CATALYST (*Continued*)

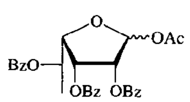
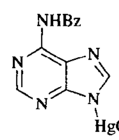
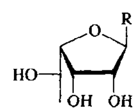
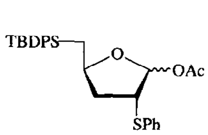
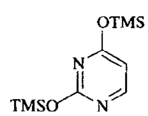
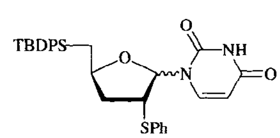
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $TiCl_4$, $Cl(CH_2)_2Cl$, reflux, 2 h 2. NaOMe, MeOH, reflux, 1 h	 (31-39)	1079
		$TiCl_4$ (1-6 eq), $Cl(CH_2)_2Cl$, rt	 (65) $\alpha:\beta = 15:85$	228, 229

TABLE VI. REACTIONS WITH BORON TRIFLUORIDE ETHERATE AS CATALYST

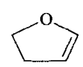
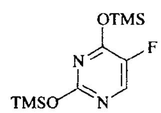
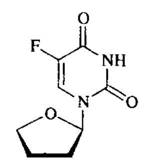
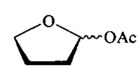
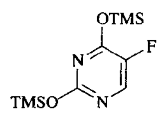
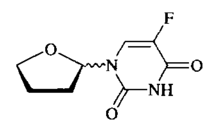
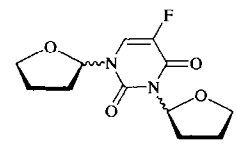
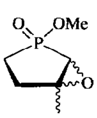
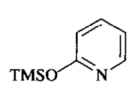
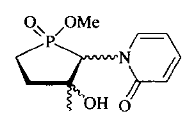
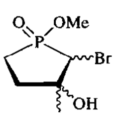
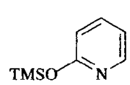
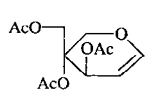
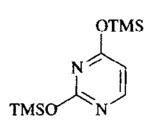
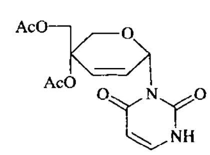
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		1. H^+ 2. BF_3•OEt_2, dioxane, rt, 3 h	 (93)	639
C_6 		BF_3•OEt_2 (1 eq), CH_2Cl_2, rt, 1 h	 (70)	528
		BF_3•OEt_2 (0.02 eq), CH_2Cl_2, rt, 1 h	 (67)	528
		BF_3•OEt_2, MeCN, reflux, 48 h	 I (15)	652
		BF_3•OEt_2 (0.5 eq), MeCN, reflux, 24 h	I (62)	652
C_{12} 		BF_3•OEt_2, EtOAc, −20°, 1 h	 (35) + β-anomer (32)	107

TABLE VI. REACTIONS WITH BORON TRIFLUORIDE ETHERATE AS CATALYST (*Continued*)

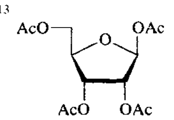
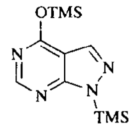
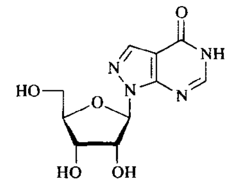
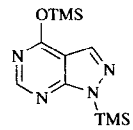
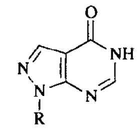
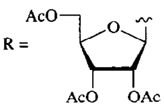
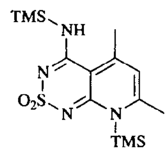
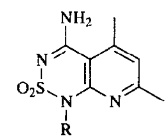
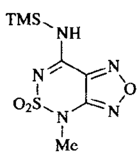
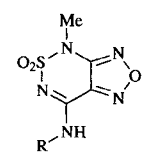
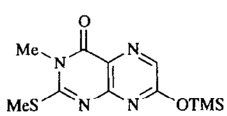
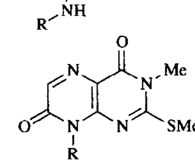
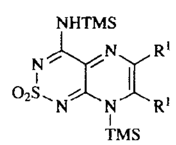
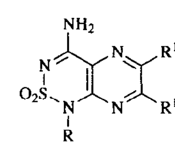
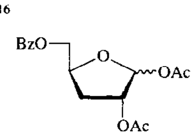
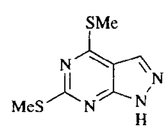
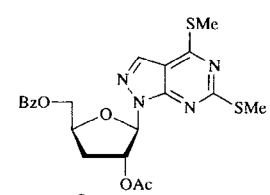
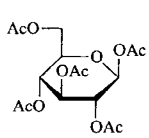
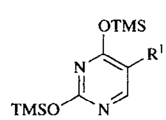
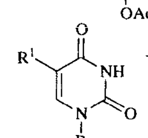
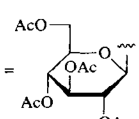
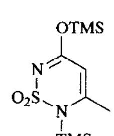
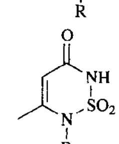
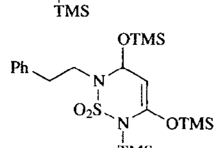
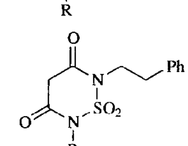
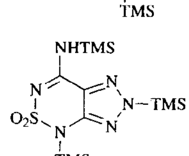
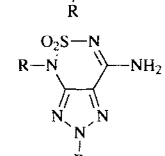
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 		1. BF_3•OEt_2, dioxane, reflux, 30 min 2. NH_3, MeOH	 (44) + α-anomer (44) + N^7-isomer (5)	1080
		BF_3•OEt_2, dioxane, reflux, 30 min	 **I** (38) R = 	1081
		BF_3•OEt_2, dioxane, 60°, 24 h	**I** (—) N^2 and N^5 ribosides + N^1,N^5-bis(riboside) 2:2:1	735
		BF_3•OEt_2, CH_2Cl_2, rt, 4 h	 (36)	1082
		1. BF_3•OEt_2, CH_2Cl_2, rt, 6 h 2. Zn, AcOH, reflux, 4 h	 (40)	1083
		BF_3•OEt_2, CH_2Cl_2, rt, 2 h	 (53)	1084
		BF_3•OEt_2, CH_2Cl_2, rt, 4 h	 R^1: H (12) + N^8-isomer (7); Ph (40)	1085
C_{16} 		BF_3•OEt_2, MeCN	 (60) + N^2-β-isomer (2)	1086, 1087
		BF_3•OEt_2, HMPA, 190°, 15 min	 R^1: H (26); Me (14) R = 	102
		BF_3•OEt_2, CH_2Cl_2, rt, 4 h	 (45) + bis(riboside) (32)	1088
		BF_3•OEt_2, CH_2Cl_2, rt, 4 h	 (79)	1089
		BF_3•OEt_2, MeCN, rt, 12 h	 (35)	1090

TABLE VI. REACTIONS WITH BORON TRIFLUORIDE ETHERATE AS CATALYST (*Continued*)

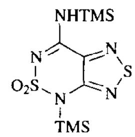
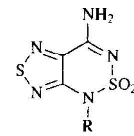
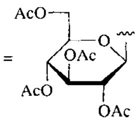
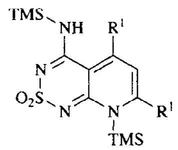
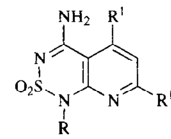
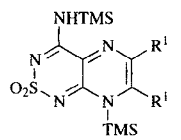
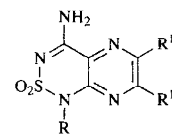
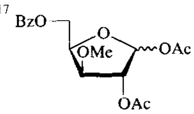
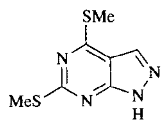
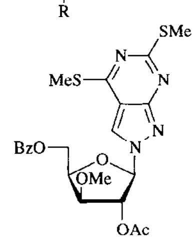
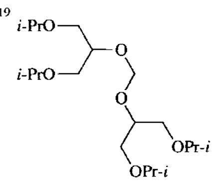
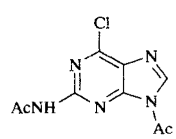
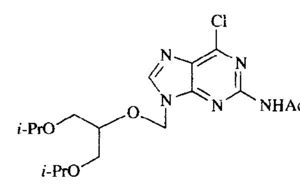
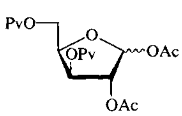
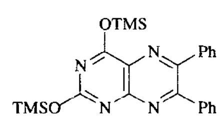
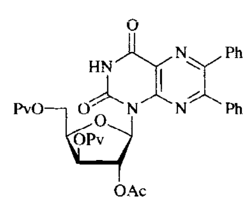
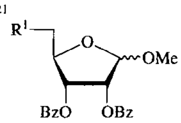
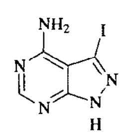
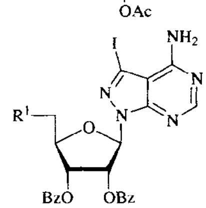
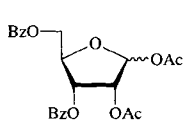
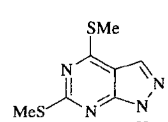
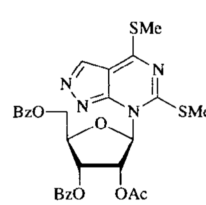
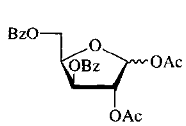
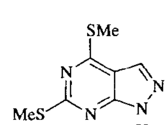
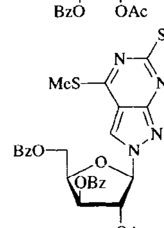
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$BF_3{\bullet}OEt_2$, MeCN, rt, 12 h	 (64) R = 	1090
		$BF_3{\bullet}OEt_2$, CH_2Cl_2, rt, 4 h	 R^1: Me (4); Ph (66)	1082
		$BF_3{\bullet}OEt_2$, CH_2Cl_2, rt, 4 h	 R^1: H (16); Me (81); Ph (81)	1091
C_{17} 		$BF_3{\bullet}OEt_2$, MeCN	 (56)	1086
C_{19} 		$BF_3{\bullet}OEt_2$, *N*-methylpyrrolidone, 100°, 4 h	 (63)	521
C_{19} 		$BF_3{\bullet}OEt_2$, EtOAc, rt, 2 h	 (72)	1029
$C_{20\text{-}21}$ 		$BF_3{\bullet}OEt_2$, $MeNO_2$, reflux, 2 h	 R^1: F (52); Cl (82); N_3 (32); H (43)	519
C_{23} 		$BF_3{\bullet}OEt_2$, MeCN	 (60) N^1:N^3 = 6:1	1086
		$BF_3{\bullet}OEt_2$, MeCN	 (40) + N^1-α-isomer (20)	1086

TABLE VI. REACTIONS WITH BORON TRIFLUORIDE ETHERATE AS CATALYST (*Continued*)

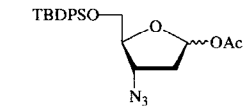
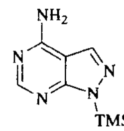
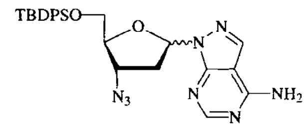
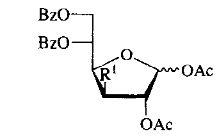
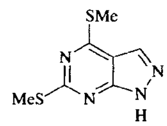
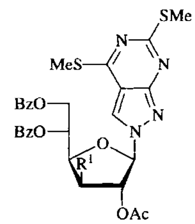
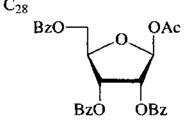
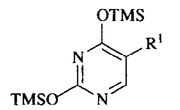
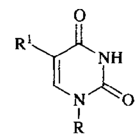
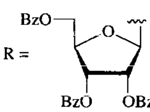
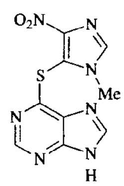
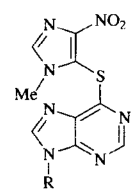
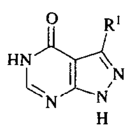
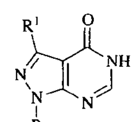
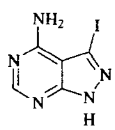
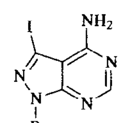
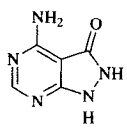
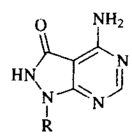
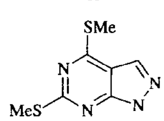
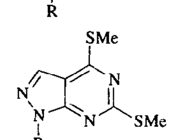
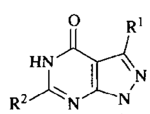
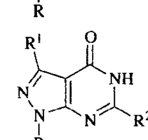
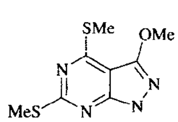
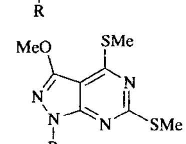
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$BF_3{\bullet}OEt_2$, dioxane, rt, 12 h	 (65) α:β = 1:3	749
C_{25} 		$BF_3{\bullet}OEt_2$, MeCN	 R^1: OMe (52) + α-isomer (10); OMs (30) + N^1-α-isomer (10)	1086
C_{28} 		$BF_3{\bullet}OEt_2$, HMPA, 190°, 15 min	 R^1: H (14); Me (67); R = 	102
		$BF_3{\bullet}OEt_2$, $MeNO_2$, reflux, 45 min	 (30)	1092
		$BF_3{\bullet}OEt_2$, $MeNO_2$, reflux	 R^1: Br 90 min (45); CN 90 min (45)	1055 1055
		$BF_3{\bullet}OEt_2$, PhCN, 160-180°, 15 min	R^1 = CN (52)	1055
		$BF_3{\bullet}OEt_2$, $MeNO_2$, reflux, 2 h	 (86)	519
		$BF_3{\bullet}OEt_2$, $MeNO_2$, reflux, 15 min	 (37)	1095
		$BF_3{\bullet}OEt_2$, solvent, reflux, 1 h	 Solvent / α-anomer: $MeNO_2$ (60) (10); MeCN (58) (12); CH_2Cl_2 (40) (5)	1094
		$BF_3{\bullet}OEt_2$, $MeNO_2$, reflux, time	 R^1 / R^2 / time: Me Br 5 min (62); OMe SMe 40 min (78); OEt SMe 20 min (61)	1056 1093 1095
		$BF_3{\bullet}OEt_2$, solvent, reflux, 20 min	 (45)	1095

TABLE VI. REACTIONS WITH BORON TRIFLUORIDE ETHERATE AS CATALYST (*Continued*)

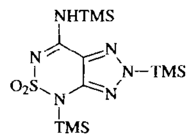
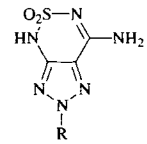
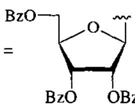
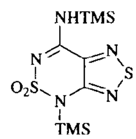
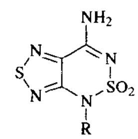
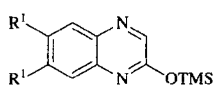
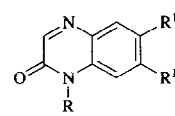
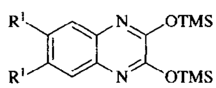
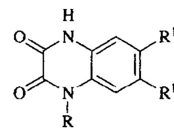
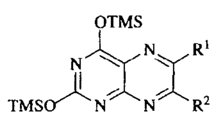
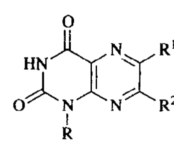
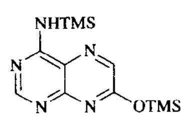
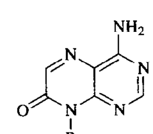
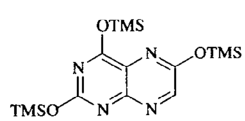
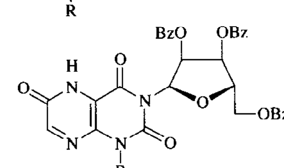
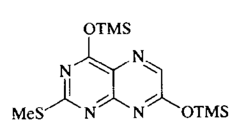
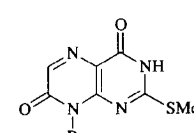
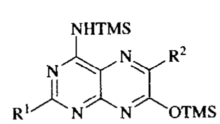
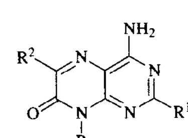
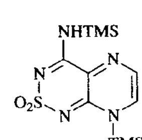
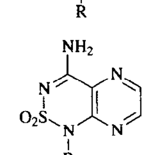
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$BF_3 \cdot OEt_2$, MeCN, rt, 12 h	 (35) R = 	1090
		$BF_3 \cdot OEt_2$, MeCN, rt, 12 h	 (59)	1090
		$BF_3 \cdot OEt_2$, CH_2Cl_2, rt, time	 R^1 / time: H, 1 h (19); Cl, 1 h (13); Me, 2.5 h (36)	1096
		$BF_3 \cdot OEt_2$, CH_2Cl_2, rt, time	 R^1 / time: H, 1 h (40); Cl, 1 h (36); Me, 1 h (25)	1096
		$BF_3 \cdot OEt_2$		
	R^1 H, R^2 H	C_6H_6, rt, 1 h	(30) + N^3-isomer (19) + N^1,N^3-bis(riboside) (20)	1097
	R^1 p-ClC_6H_4, R^2 H	EtOAc, 20°, 30 min	(53)	104
	R^1 H, R^2 p-ClC_6H_4	EtOAc, 20°, 30 min	(68) + N^3-β-isomer (5)	104
		$BF_3 \cdot OEt_2$, $CHCl_3$, rt, 3 h	 (53)	1098
		$BF_3 \cdot OEt_2$, CH_2Cl_2, rt, 2 h	 (65)	1099
		$BF_3 \cdot OEt_2$, CH_2Cl_2, rt, 4 h	 (82)	1084
		$BF_3 \cdot OEt_2$, CH_2Cl_2, rt, time	 R^1 / R^2 / time: Ph, H, 3 h (75); H, Ph, 8 h (40)	1098
		$BF_3 \cdot OEt_2$, CH_2Cl_2, rt, 4 h	 (31) + N^8-isomer (9)	1085

TABLE VI. REACTIONS WITH BORON TRIFLUORIDE ETHERATE AS CATALYST (*Continued*)

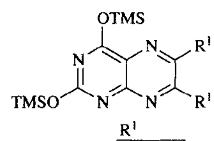
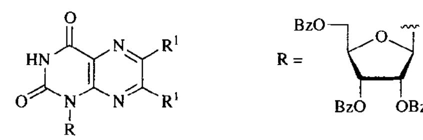
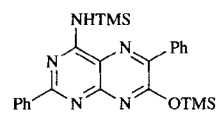
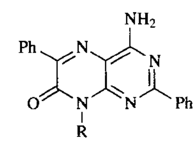
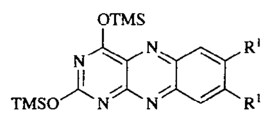
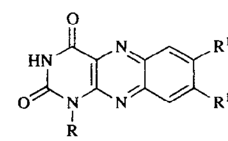
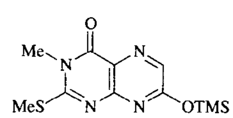
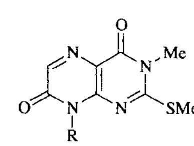
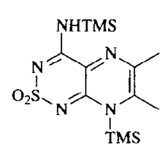
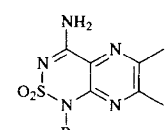
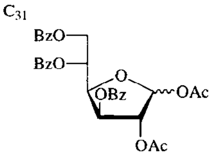
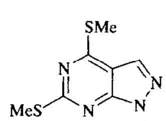
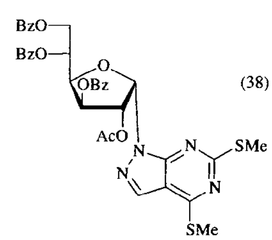
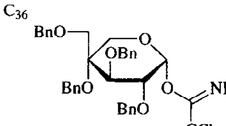
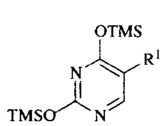
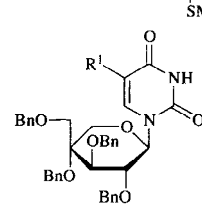
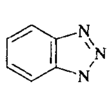
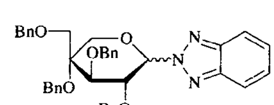
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$BF_3•OEt_2$		
	R^1			
	Me	C_6H_6, rt, 1 h	(25) + N^3-isomer (19) + N^1,N^3-bis(riboside) (26)	1097
	Ph	C_6H_6, rt, 1 h	(20) + N^3-isomer (17) + N^1,N^3-bis(riboside) (56)	1097
	Ph	C_6H_6, rt, 4 h	(9) + N^3-isomer (64) + N^1,N^3-bis(riboside) (9)	1100
	Ph	EtOAc, rt, 3 h	(71)	1100
	p-ClC_6H_4	CCl_4, 20°, 1 h	(45) + N^3-β-isomer (20) + N^3-α-isomer (11)	104
	p-ClC_6H_4	EtOAc, 20°, 1 h	(69) + N^3-isomer (2)	104
		$BF_3•OEt_2$, CH_2Cl_2, rt, 24 h	 (59)	1098
		$BF_3•OEt_2$, EtOAc, rt, 2 h	 R^1: H (55); Me (54)	103
		$BF_3•OEt_2$, C_6H_6, rt, 4 h	R^1 = Me, (34) + N^3-isomer (19) + N^1,N^3-bis(isomer) (23)	103
		$BF_3•OEt_2$, CH_2Cl_2, rt, 2 h	 (75)	1084
		$BF_3•OEt_2$, CH_2Cl_2, rt, 4 h	 (81)	1085
C_{31} 		$BF_3•OEt_2$, MeCN	 (38) + N^2-β-isomer (30)	1086
C_{36} 		$BF_3•OEt_2$, CH_2Cl_2, rt, 2 h	 R^1: H (62); Me (61)	1101
		$BF_3•OEt_2$, CH_2Cl_2, −22°, 2 h	 (51) α:β = 1:9 + N^1-β-isomer (24)	1101

TABLE VII. REACTIONS WITH MISCELLANEOUS FRIEDEL-CRAFTS CATALYSTS

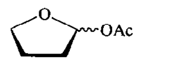
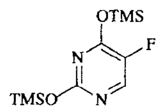
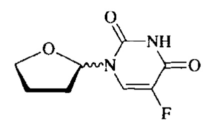
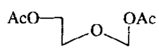
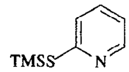
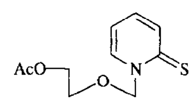
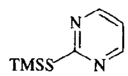
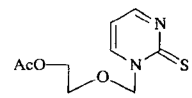
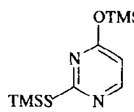
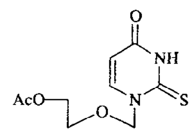
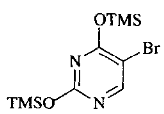
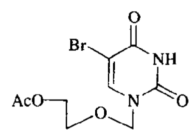
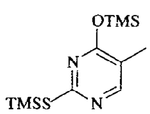
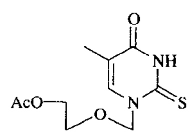
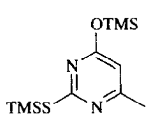
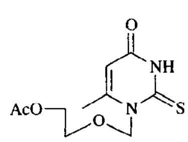
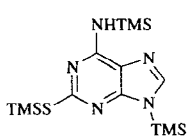
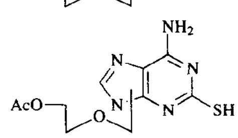
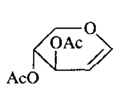
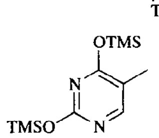
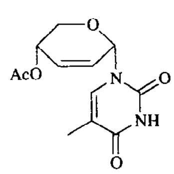
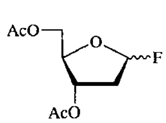
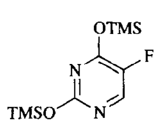
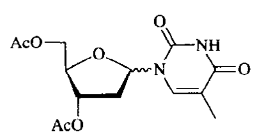
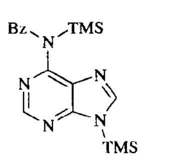
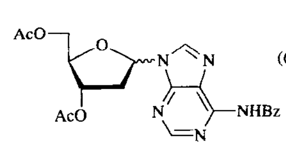
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		$SbCl_5$, CH_2Cl_2, rt, 0.1 h	 (8)	528
C_7				
		ZnI_2, DMF, 100°, 3 h	 (67)	113
		ZnI_2, DMF, 100°, 3 h	 (76)	113
		ZnI_2, DMF, 100°, 4 h	 (73)	113
		ZnI_2, DMF, 100°, 7 h	 (60)	113
		ZnI_2, DMF, 100°, 5 h	 (51)	113
		ZnI_2, DMF, 100°, 7 h	 (35)	113
		ZnI_2, DMF, 100°, 7 h	 (55) N^7:N^9 = 1:3	113
C_9				
		$LiClO_4$, $Cl(CH_2)_2Cl$, $Ph_3C^+ClO_4^-$, rt, 10 min	 (75)	309
		SiF_4, MeCN, −20°, 2 h	 (76) α:β = 40:60	118
		SiF_4, MeCN, −20°, 2 h	 (64) α:β = 50:50	118

TABLE VII. REACTIONS WITH MISCELLANEOUS FRIEDEL-CRAFTS CATALYSTS (*Continued*)

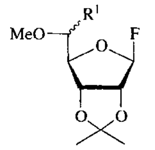
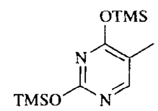
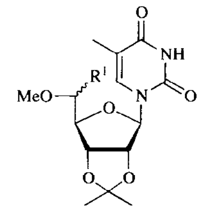
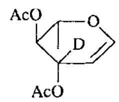
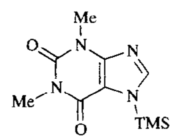
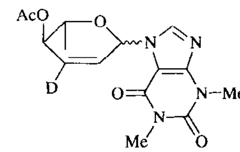
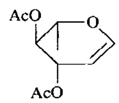
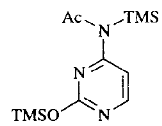
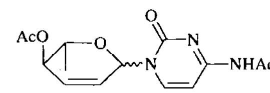
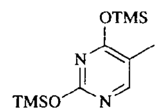
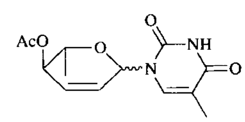
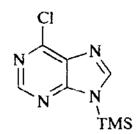
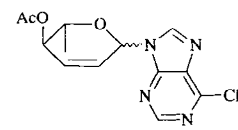
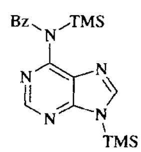
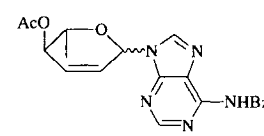
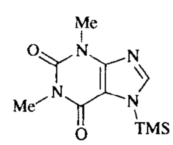
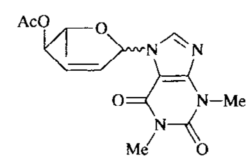
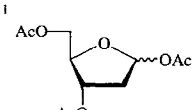
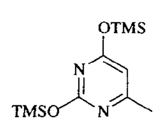
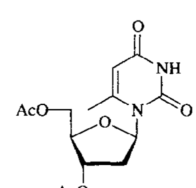
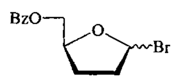
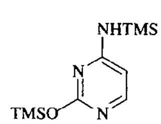
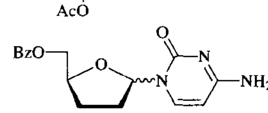
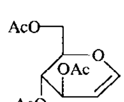
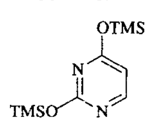
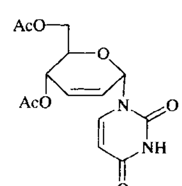
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		SiF_4, MeCN	 R^1: F, 0° (40); H, rt, 10 min (33)	118a
C_{10}				
		$Ph_3C^+ClO_4^-$, $Cl(CH_2)_2Cl$, rt, 5 min	 (72) α:β = 1:1	123
		$Ph_3C^+ClO_4^-$, $Cl(CH_2)_2Cl$, MS, rt, 3 h	 (81) α:β = 52:48	123
		$Ph_3C^+ClO_4^-$, $Cl(CH_2)_2Cl$, MS, rt, 3 h	 (63) α:β = 45:55	123
		$Ph_3C^+ClO_4^-$, $Cl(CH_2)_2Cl$, rt, 5 min	 (71) α:β = 54:46	123
		$Ph_3C^+ClO_4^-$, $Cl(CH_2)_2Cl$, rt, 5 min	 (61) α:β = 54:46	123
		$Ph_3C^+ClO_4^-$, $Cl(CH_2)_2Cl$, rt, 5 min	 (78) α:β = 54:46	123
C_{11}				
		1. $SbCl_5$, EtOAc, 20°, 20 min 2. NaOMe, MeOH	 (17) + α-anomer (16) + N^3-β-isomer (17) + N^3-α-isomer (16)	109
C_{12}				
		TMSBr, CH_2Cl_2, −78° to rt	 (44) α:β = 1:1	1102
		$SbCl_5$, EtOAc, rt, 15 min, or 23°, 5 min	 (40) + β-anomer (24)	108, 1103

TABLE VII. REACTIONS WITH MISCELLANEOUS FRIEDEL-CRAFTS CATALYSTS (*Continued*)

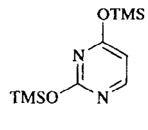
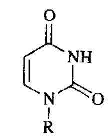
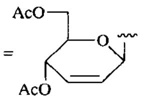
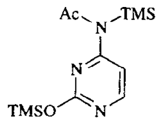
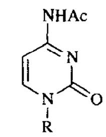
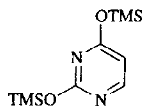
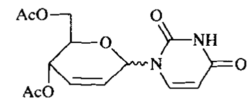
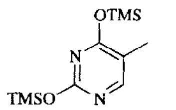
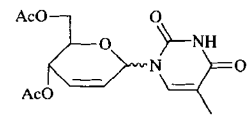
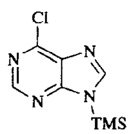
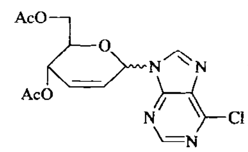
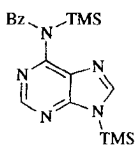
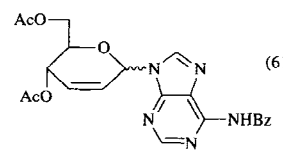
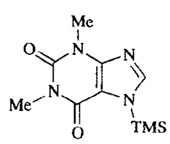
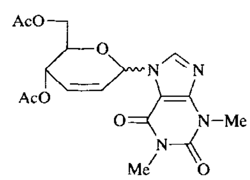
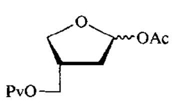
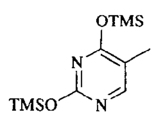
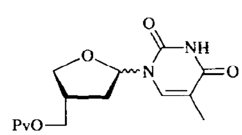
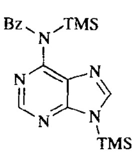
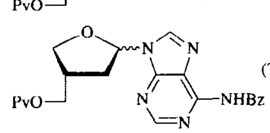
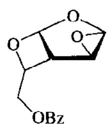
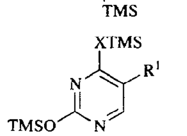
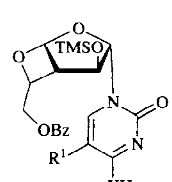
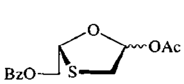
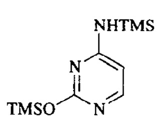
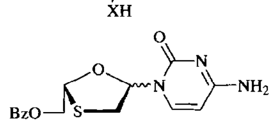
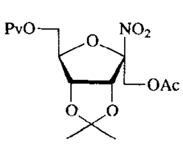
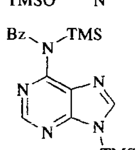
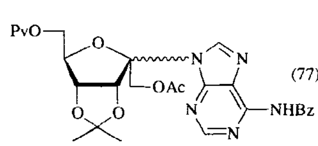
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SbCl_5$, EtOAc, rt, 5 min	 (26) + α-anomer (23) R = 	107
		$LiClO_4$, $Cl(CH_2)_2Cl$, $Ph_3C^+ClO_4^-$, rt, 3 h	 (56)	123
		$SnCl_2$, MeCN	 (78)	1104
		$LiClO_4$, $Cl(CH_2)_2Cl$, $Ph_3C^+ClO_4^-$, rt, 3 h	 (63) α:β = 48:52	123
		$Ph_3C^+ClO_4^-$, $Cl(CH_2)_2Cl$, rt, 5 min	 (76) α:β = 58:42	123
		$Ph_3C^+ClO_4^-$, $Cl(CH_2)_2Cl$, rt, 5 min	 (61) α:β = 50:50	123
		$Ph_3C^+ClO_4^-$, $Cl(CH_2)_2Cl$, rt, 5 min	 (61) α:β = 49:51	123
		TMSI, MeCN, −5 - 0°, 1 h	 (93) α:β = 5:4	139a
		TMSI, MeCN, −5°, 2 h	 (72) α:β = 2:5	139a
C_{13} 		$ZnCl_2$, THF, rt, 18 h	 R^1 X H NH (58) Me O (66)	1105
		TMSI, $Cl(CH_2)_2Cl$	 (83) α:β = 1.3:1	1106
		$SnCl_2$, MeCN, 8°, 30 min	 (77) α:β = 1:3.5	106

TABLE VII. REACTIONS WITH MISCELLANEOUS FRIEDEL-CRAFTS CATALYSTS (*Continued*)

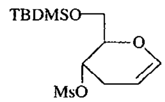
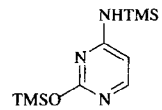
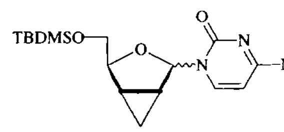
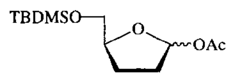
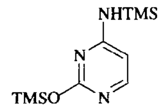
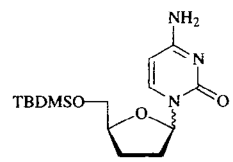
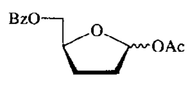
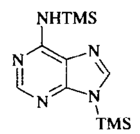
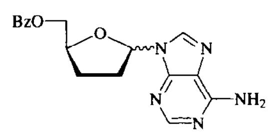
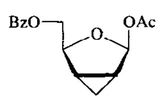
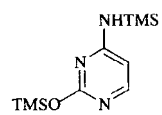
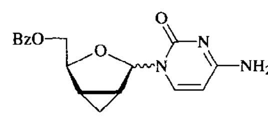
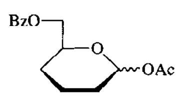
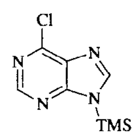
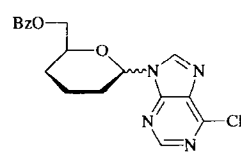
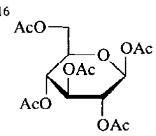
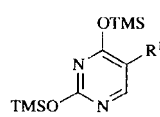
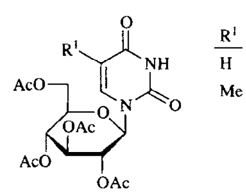
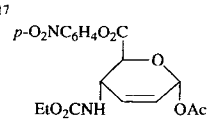
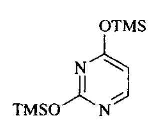
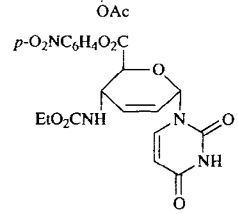
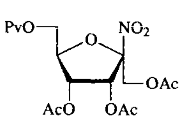
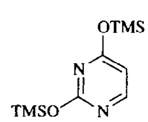
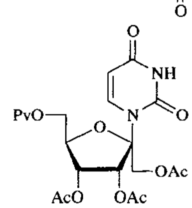
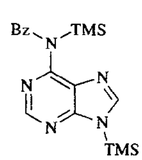
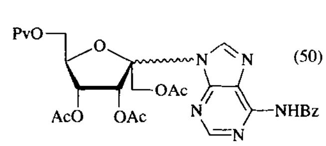
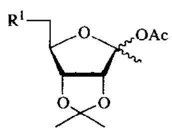
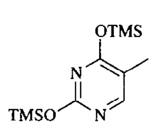
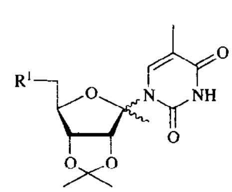
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$EtAlCl_2$, MeCN, reflux	 (81) α:β = 1:1	115, 312a
		$EtAlCl_2$, CH_2Cl_2, 27°, 2.5 h	 (42) + α-anomer (18)	114, 287
C_{14}				
		TMSBr, CH_2Cl_2, 0° to rt	 (63)	1102
C_{15}				
		$EtAlCl_2$, PhMe, CH_2Cl_2, rt, 40 min	 (37) α:β = 1:1	116
		TMSBr, $CHCl_3$, rt, 1 h	 (63)	1107
C_{16}				
		$SbCl_5$, DME, rt, 6 d	 R[1]: H (19); Me (38)	102
C_{17}				
		$SbCl_5$, CH_2Cl_2, 25°, 30 min	 (44)	308
		$SnCl_2$, MeCN, 60°, 30 min	 (48)	106
		$SnCl_2$, MeCN, rt, 30 min	 (50) α:β = 2:3	106
C_{17-18}				
		$EtAlCl_2$, MeCN, rt	 R[1]: BnO (86) α:β = 1:9; TBDMSO (90) α:β = 1:3	117

TABLE VII. REACTIONS WITH MISCELLANEOUS FRIEDEL-CRAFTS CATALYSTS (*Continued*)

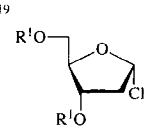
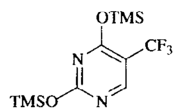
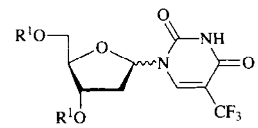
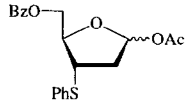
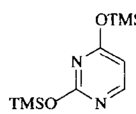
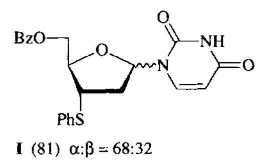
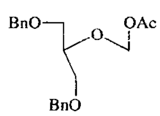
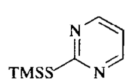
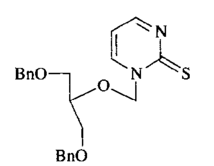
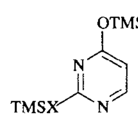
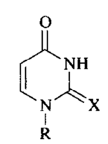
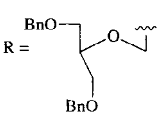
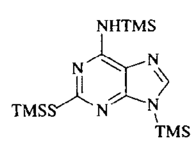
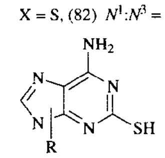
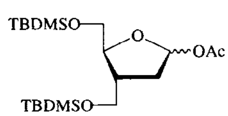
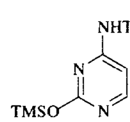
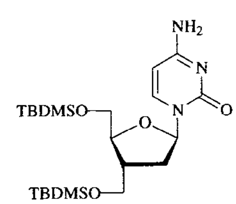
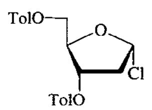
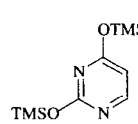
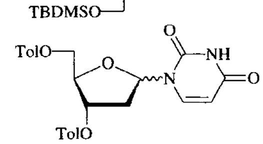
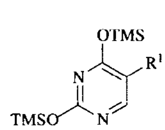
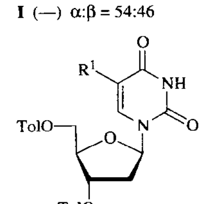
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}  R^1 = *p*-ClC_6H_4CO		$ZnCl_2$, $CHCl_3$, rt, 12 h	 I (78) α:β = 25:75	269
		$ZnCl_2$, $CHCl_3$, rt, 15 h sugar:base = 1:4	I (58) α:β = 7:93	269
		$ZnCl_2$, $CHCl_3$, rt, 15 h sugar:base = 1:2	I (78) α:β = 25:75	269
C_{20} 		TMSBr, CH_2Cl_2, rt, 12 h	 I (56) α:β = 54:46	229
		TMSBr, $HgBr_2$, CH_2Cl_2, rt, 12 h	I (81) α:β = 68:32	229
		TMSBr, $Sn(OTf)_2$, CH_2Cl_2, rt, 12 h	I (84) α:β = 65:35	229
		n-$BuSnCl_3$, CH_2Cl_2, rt, 12 h	I (83) α:β = 77:23	229
		ZnI_2, DMF, 100°, 5 h	 (71)	113
		ZnI_2, DMF, 100°, 5 h	 X: O (67); S (88); R = 	113
		ZnI_2, DMF, reflux, 5 h	X = S, (82) N^1:N^3 = 1:1	113
		ZnI_2, DMF, 100°, 7 h	 (73) N^9:N^7 = 4:1	113
		$EtAlCl_2$, $Cl(CH_2)_2Cl$, 0°, 30 min	 (74)	1108
C_{21} 		AlI_3, $Cl(CH_2)_2Cl$, 0°	 I (—) α:β = 65:35	273
		ZnI_2, EDC, rt	I (—) α:β = 49:51	273
		ZnI_2, $CDCl_3$, EDC, 0°	I (—) α:β = 54:46	273
		ZnI_2, $CHCl_3$, rt, 24 h	 R^1: NO_2 (82); Ac (76) α:β = 1:1.23	261

TABLE VII. REACTIONS WITH MISCELLANEOUS FRIEDEL-CRAFTS CATALYSTS (*Continued*)

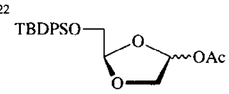
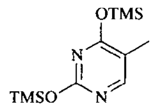
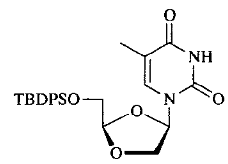
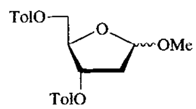
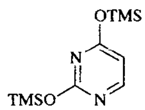
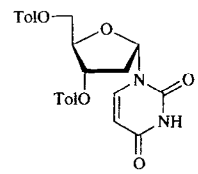
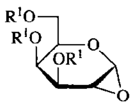
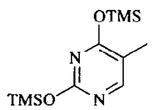
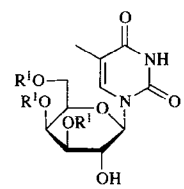
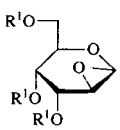
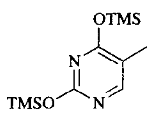
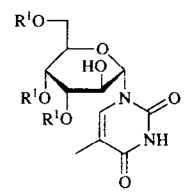
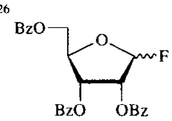
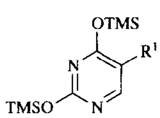
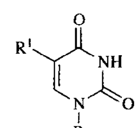
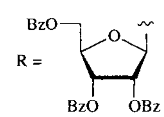
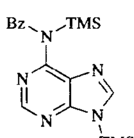
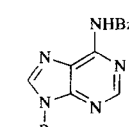
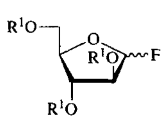
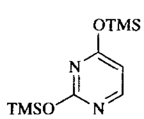
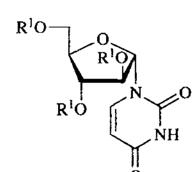
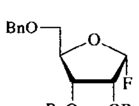
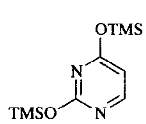
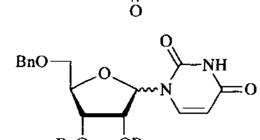
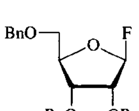
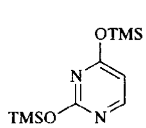
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 		$TiCl_2(OPr\text{-}i)_2$	 (40)	235
		TMSCl, NaI, MeCN	 (65)	137
C_{24}  R^1 = TBDMS		$ZnCl_2$, THF, rt, 12 h	 I (44)	112
 R^1 = TBDMS		$ZnCl_2$, THF, rt, 17 h	 (79)	112
C_{26} 		SiF_4, MeCN, 0°, 2 h	 R^1: H (90); F (86); R = 	118
		SiF_4, MeCN, 0°, 2 h	 (82)	118
		SiF_4, 0°	 R^1: Bz, MeCN, 1 h (76); Bn, CH_2Cl_2, 2 h (72); Bn, MeCN, 2 h (78)	118
		SiF_4, MeCN, rt, 2 h	 I (85) α:β = 16:84	1109
		SiF_4, MeCN, 0°, 1 h	I (85) α:β = 16:84	118
		SiF_4, CH_2Cl_2, 0°, 0.5 h	I (80) α:β = 60:40	118
		SiF_4, Et_2O, 0°, 0.5 h	I (82) α:β = 55:45	118
		SiF_4, MeCN, 0°, 1 h	I (84) α:β = 18:82	118
		SiF_4, CH_2Cl_2, 0°, 0.5 h	I (84) α:β = 68:32	118
		SiF_4, Et_2O, 0°, 0.5 h	I (78) α:β = 60:40	118

TABLE VII. REACTIONS WITH MISCELLANEOUS FRIEDEL-CRAFTS CATALYSTS (*Continued*)

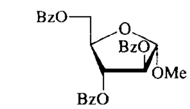
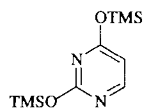
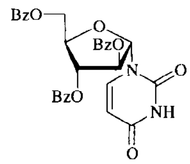
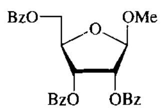
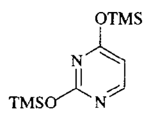
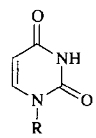
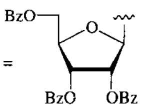
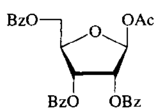
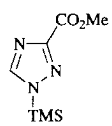
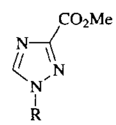
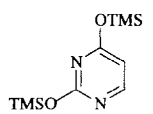
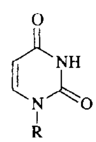
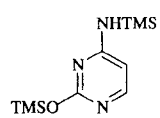
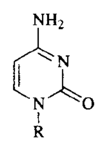
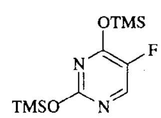
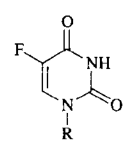
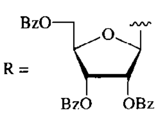
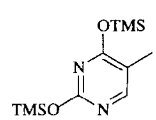
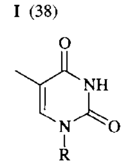
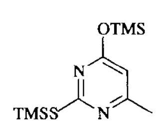
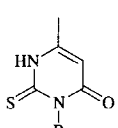
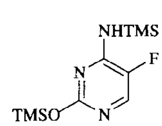
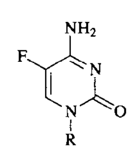
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27} 		TMSI, MeCN, 70°	 (65-70)	137
		TCS, NaI, MeCN, 70°	 (76) R = 	137
C_{28} 		TMSCl, MeCN, NaI, 24°, 20 h	 (82)	1110
		TMSI, MeCN, MS, rt	 I (89)	136
		TMSCl, MeCN, NaI, rt, 50 min	I (64-68)	137, 1111
		TMSCl, MeCN, MS, rt, 100 min	I (89)	1111
		TMSI, MeCN, MS, rt	 (81)	136
		$ZnCl_2$, MeCN, rt, 3 h	 I (42) R = 	868
		TMSCl, MeCN, NaI, MS, rt, 3 h	I (84)	135
		$AlCl_3$, MeCN, rt, 3 h	I (38)	514b
		TMSCl, MeCN, NaI, MS, rt, 3 h	 I (85)	135
		$SbCl_5$, DME, rt, 3.5 h	I (36)	102
		$AlCl_3$, MeCN, 22°, 4 h	 (5) + *S*-riboside (62)	89a
		TMSCl, MeCN, NaI, MS, rt, 3 h	 (83)	135

TABLE VII. REACTIONS WITH MISCELLANEOUS FRIEDEL-CRAFTS CATALYSTS (*Continued*)

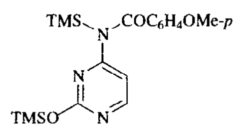
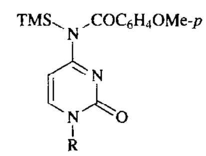
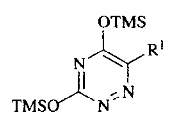
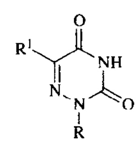
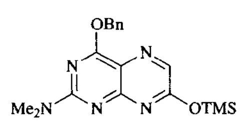
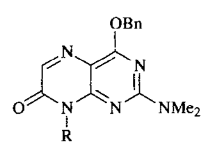
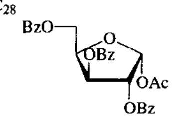
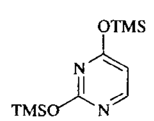
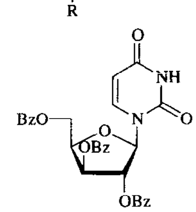
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSCl, MeCN, NaI, MS, rt, 3 h	 (73)	135
		TMSI, MeCN, rt, 4-5 h		
	R^1			
	H		(83)	139
	Br		(80)	139
	NMe_2		(21)	139
	SMe		(44)	139
	$SCHF_2$		(83)	139
	SCF_3	20°, 4-6 h	(73-80)	1111a
		$ZnCl_2$, 140-150°, 75 min	 (9)	1112
C_{28} 		TMSI, MeCN, 70°, or TMSI, rt	 (58)	137

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS

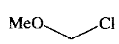
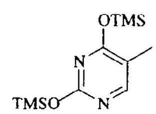
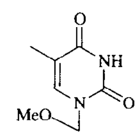
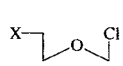
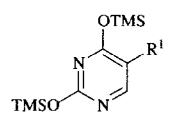
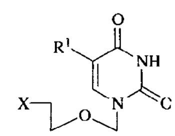
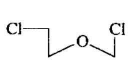
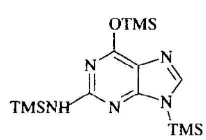
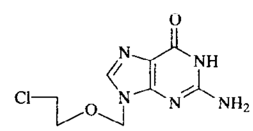
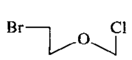
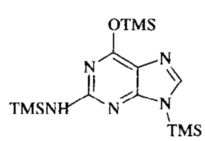
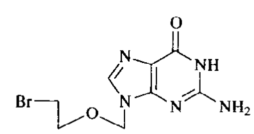
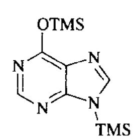
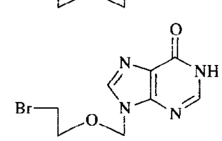
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
		Bu_4NI, CH_2Cl_2, reflux, 2 h	 (54)	399
C_3				
		Bu_4NF, THF, C_6H_6, reflux, 3 h		1113
X	R^1			
Cl	H		(80-90)	
Cl	Me		(80-90)	
Br	H		(80-90)	
Br	Me		(80-90)	
		Bu_4NF, THF, C_6H_6, reflux, 30 h	 (90)	1113
		Bu_4NF, THF, C_6H_6, reflux, 3 h	 (95)	1113
		Bu_4NF, THF, C_6H_6, reflux, 3 h	 (80)	1113

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

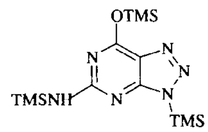
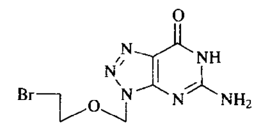
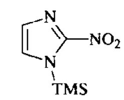
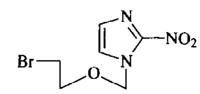
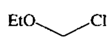
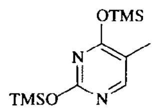
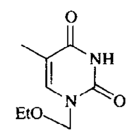
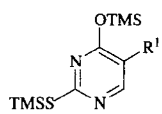
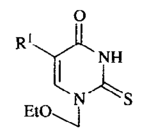
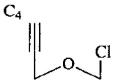
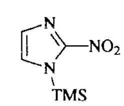
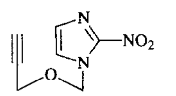
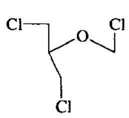
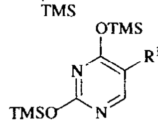
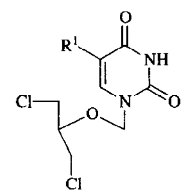
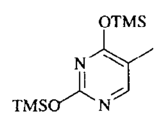
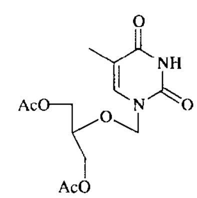
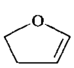
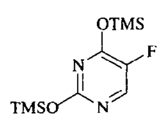
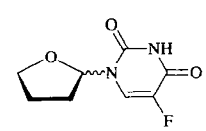
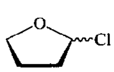
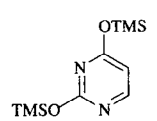
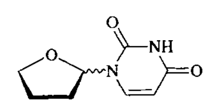
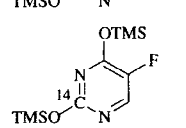
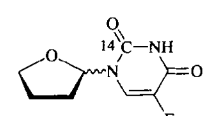
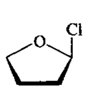
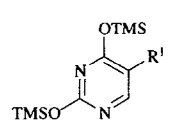
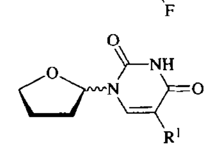
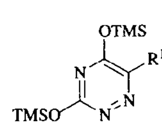
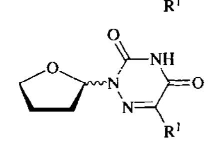
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		Bu_4NF, THF, C_6H_6, reflux, 3 h	 (98)	1113
		Bu_4NF, $Cl(CH_2)_2Cl$ rt, 16 h	 (73)	1114
		Bu_4NI, CH_2Cl_2, reflux, 2 h	 (62)	399
		CsI, MeCN, reflux, 2 h	 R^1: Et (37); *i*-Pr (31); *c*-C_3H_5 (43)	399
C_4 		Bu_4NF, $Cl(CH_2)_2Cl$ rt, 16 h	 (76)	1114
		Bu_4NI, CH_2Cl_2, reflux, 45 min	 R^1: H (80); F (88); Br (81); I (67)	786
		1. Bu_4NI, CH_2Cl_2, 24°, 12 h 2. KOAc, DMF	 (42)	1115
		1. H^+ 2. NaI, MeCN, reflux 4 h	 (90)	639
		CH_2Cl_2, 24°, 3 h	 (65)	1116
		1. CH_2Cl_2, MS, rt, 1 h 2. NH_3, MeOH, rt, 1 h	 (80)	1117
		C_6H_6, –20°, 4 h	 R^1: Br (51); Me (66)	1118
		C_6H_6, –20°, 4 h	 R^1: H (—); Br (—); Me (—)	1118

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

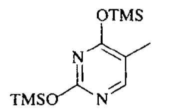
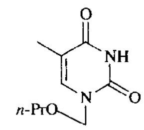
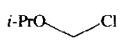
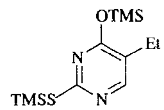
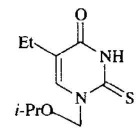
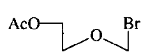
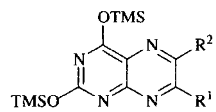
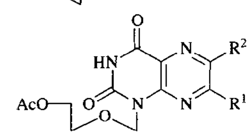
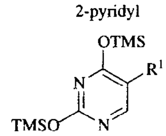
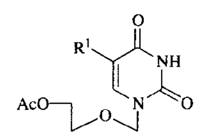
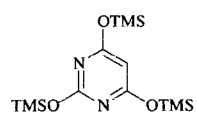
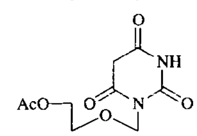
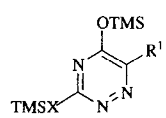
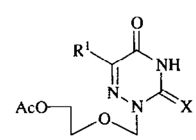
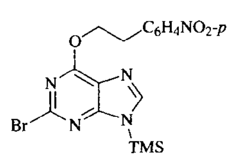
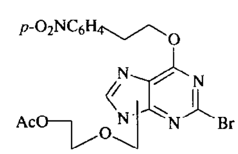
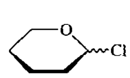
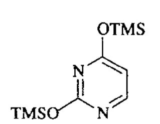
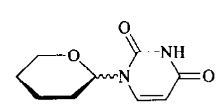
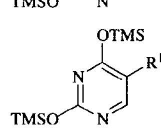
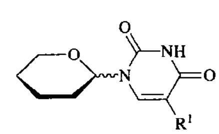
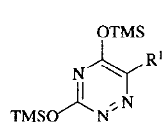
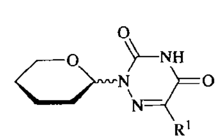
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		Bu_4NI, CH_2Cl_2, reflux, 2 h	 (63)	399
		CsI, MeCN, reflux, 2 h	 (25)	399
		Bu_4NI, MeCN, rt, 4-5 h		1119
	R^1 / R^2			
	H / H		(53)	
	Ph / H		(66)	
	p-ClC_6H_4 / H		(52)	
	Me / Me		(62)	
	Ph / Ph		(60)	
	2-pyridyl / 2-pyridyl		(55)	
		MeCN, rt, 2 d	 R^1: Bn (44); OTf (73)	655; 1120
		MeCN, reflux, 6 h	 (73)	1121
		MeCN, rt		1122
	X / R^1			
	O / Me		(62)	
	S / Me		(58)	
	O / Ph		(87)	
	S / Ph		(77)	
	O / Bn		(75)	
	S / Bn		(61)	
		MeCN, reflux, 1 h	 (76) N^7:N^9 = 1:99	143
		CH_2Cl_2, rt, 3.5 h	 (65)	1116
		C_6H_6, −20°, 4 h	 R^1: H (—); F (—); Cl (—); I (—); Me (—)	1118
		C_6H_6, −20°, 4 h	 R^1: H (—); Br (—); Me (—)	1118

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

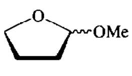
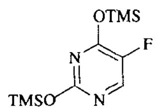
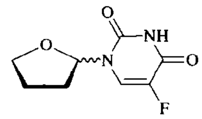
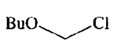
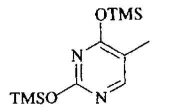
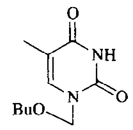
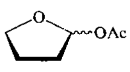
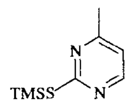
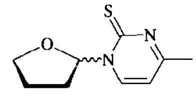
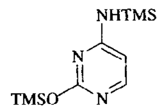
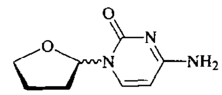
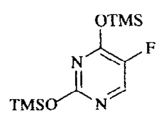
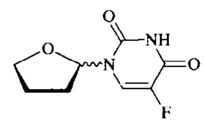
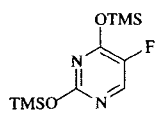
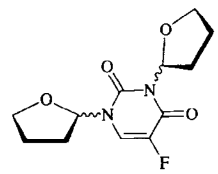
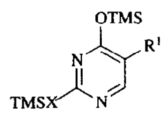
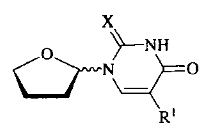
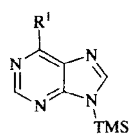
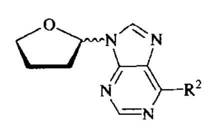
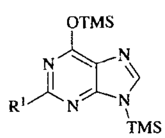
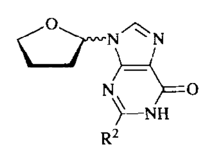
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		NaI, MeCN	 2.5 h, 160° (77); 5 h, 60-80° (84)	1123; 1124
		Bu_4NI, CH_2Cl_2, reflux, 2 h	 (49)	399
C_6				
		CsCl, MeCN, 25°, 1.5 h	 (91)	401
		CsCl, MeCN, 25°, 25 h	 (83)	401
		NaI (1 eq), MeCN, rt, 9 h	 **I** (81)	528
		NaI, MeCN, 50-60°, 2 h	**I** (95)	394
		NaI (1 eq), MeCN, 60°, 0.5 h	 (78)	528
		CsCl, MeCN, 25°, 3 h		401
	X: O, R^1: H		(74) + N^1,N^3-bisproduct	
	X: O, R^1: F		(87)	
	X: O, R^1: Br		(88)	
	X: O, R^1: NH_2		(50)	
	X: O, R^1: Me	50-55°	(73)	
	X: S, R^1: Me	50-55°	(96)	
		CsCl, MeCN		401
	R^1: Cl	25°, 3 h	R^2: Cl (96)	
	R^1: SMe	25°, 1.5 h	R^2: SMe (98)	
	R^1: NHTMS	25°, 5 h	R^2: NH_2 (92)	
		CsCl, MeCN, 25°, 4 h	 R^1: H, R^2: H (97); R^1: TMSNH, R^2: NH_2 (50)	401

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

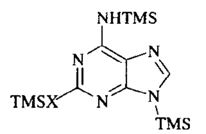
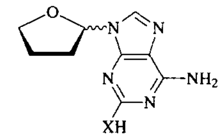
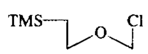
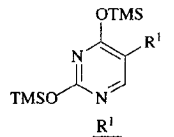
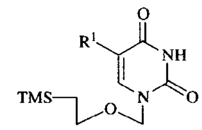
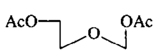
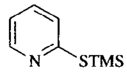
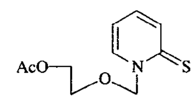
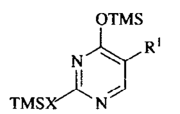
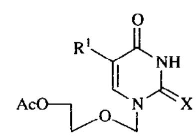
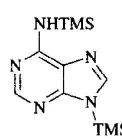
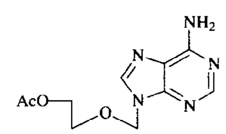
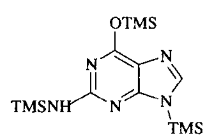
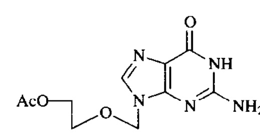
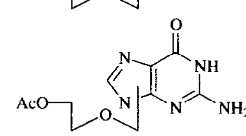
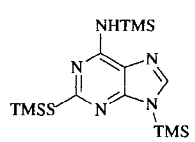
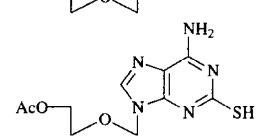
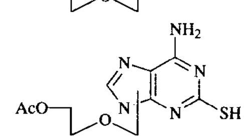
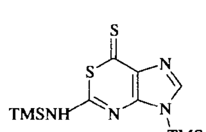
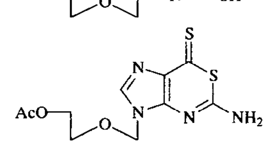
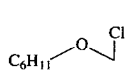
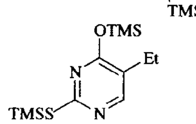
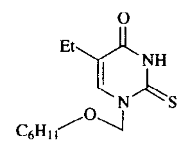
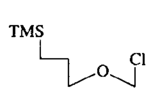
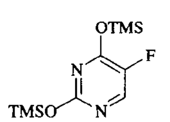
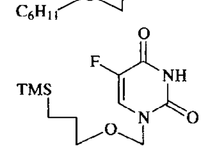
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		CsCl, MeCN, 25°, 4 h	 X: S (70); NH (98)	401
		Bu_4NI		
	R^1			
	F	MeCN, 20°, 10 min	(43)	1125
	Me	CH_2Cl_2, reflux, 2 h	(87)	399
C_7				
		CsI, MeCN, reflux, 2 h	 (76)	400
		CsI, MeCN, reflux	 X, R^1: O, H, 3 h (75); S, H, 1 h (96); O, F, 4 h (51); S, Me, 12 h (80)	400
		CsI, MeCN, reflux, 2 h	 (70)	400
		CsI, MeCN, reflux, 3 h	 (72)	400
		CsI, MeCN, reflux,12 h	 (47) N^9:N^7 = 10:1	400
		CsI, MeCN, reflux, 2 h	 (92)	400
		CsI, MeCN, reflux,12 h	 (42) N^9:N^7 = 7:1	400
		CsI, MeCN, reflux, 4 h	 (18) + N^7-isomer (15)	1126
		CsI, MeCN, reflux, 2 h	 (34)	399
		NaI, MeCN, 20°, 10 min	 (62)	1125

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

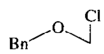
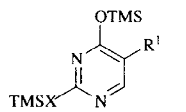
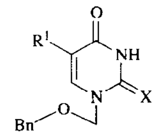
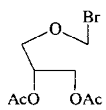
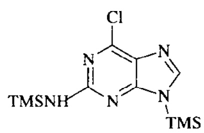
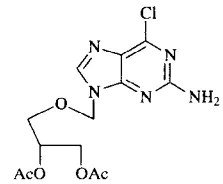
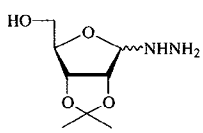
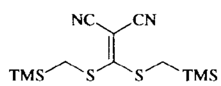
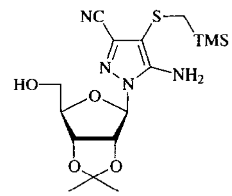
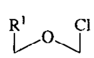
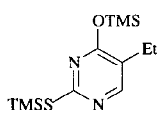
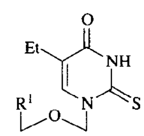
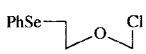
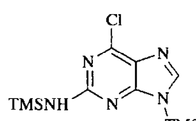
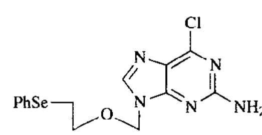
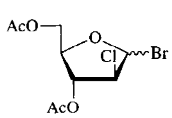
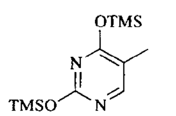
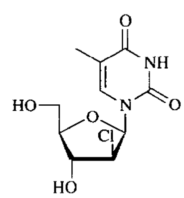
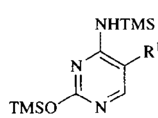
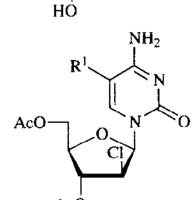
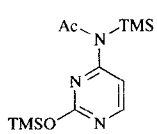
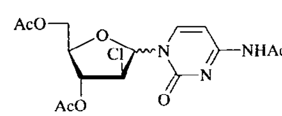
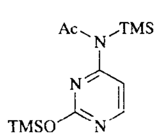
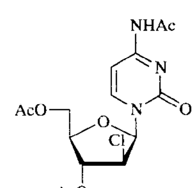
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		Reflux, 2 h		399
	X / R^1			
	O / Me	Bu_4NI, CH_2Cl_2	(86)	
	S / Et	CsI, MeCN	(36)	
	S / *i*-Pr	CsI, MeCN	(31)	
		PhMe, reflux, 18 h	 (52)	1127
		EtOH, reflux, 10 h	 (34)	447
		CsI, MeCN, reflux, 2 h	 R^1: *p*-ClC_6H_4 (16); Ph (32); C_6H_{11} (36)	399
C_9				
		$Hg(CN)_2$, C_6H_6, reflux, 30 min	 (63)	650
		1. CH_2Cl_2, rt, 48 h 2. HCl, MeOH	 (33)	1128
		CH_2Cl_2, rt, 7 d	 R^1: Br (61); I (—); Me (—)	1128
		CH_2Cl_2, rt	 (65) α:β = 1:6	219
		MeCN, rt	 (22) + α-anomer (20)	219

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

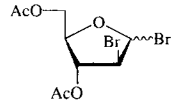
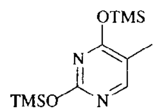
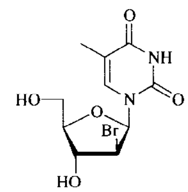
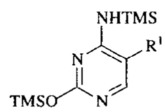
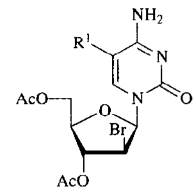
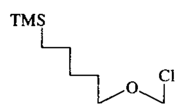
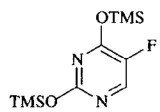
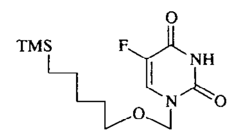
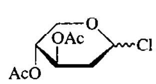
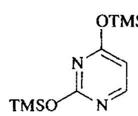
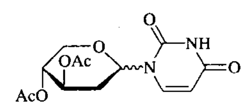
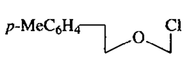
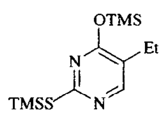
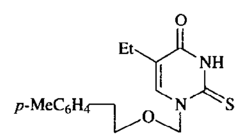
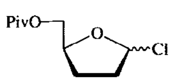
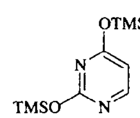
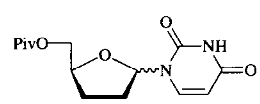
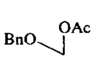
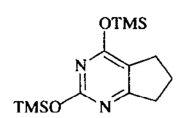
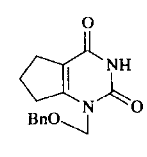
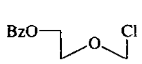
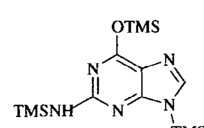
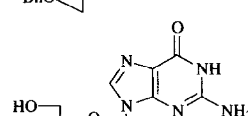
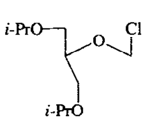
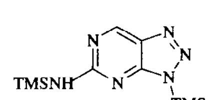
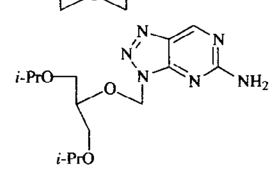
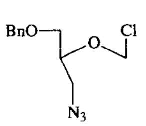
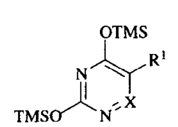
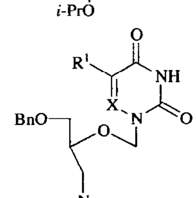
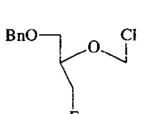
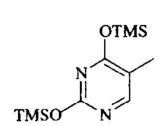
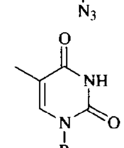
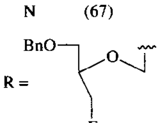
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CH_2Cl_2, rt, 48 h 2. HCl, MeOH	 (—)	1128
		CH_2Cl_2, rt, 48 h	 R^1: H (—); Me (—); Br (28); I (—)	1128
		NaI, MeCN, 20°, 10 min	 (73)	1125
		HgO, $HgBr_2$, C_6H_6, 80-100°, 5 h	 (88)	927
C_{10}				
		CsI, MeCN, reflux, 2 h	 (23)	399
		Py, $CHCl_3$, rt, 12 h	 **I** (72) α:β = 34:66	276
		$CHCl_3$, rt, 12 h	**I** (33) α:β = 38:62	276
		CsI, MeCN, reflux, 2 h	 (11)	656
		Bu_4NF, THF, C_6H_6, reflux, 3 h	 (92)	1113
		Et_3N, PhMe, 90°, 18 h	 (40)	1129
C_{11}				
		MeCN, rt, 48 h	 R^1, X: H, CH (55); Me, CH (58); H, N (51); Me, N (52); Ph, N (66); Bn, N (67)	1130
		$Hg(CN)_2$, C_6H_6, reflux 1 h	 (50) R = 	1131

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

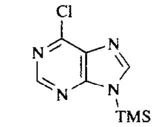
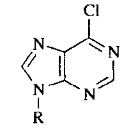
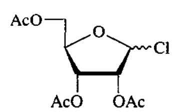
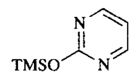
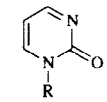
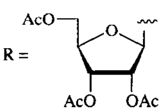
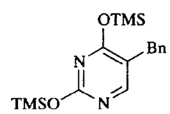
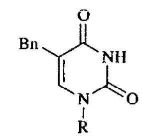
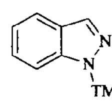
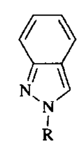
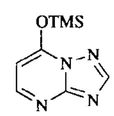
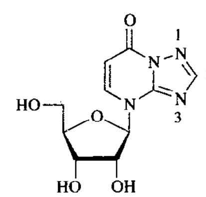
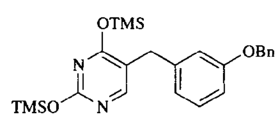
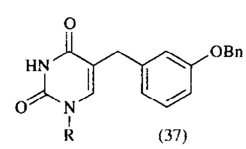
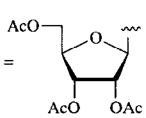
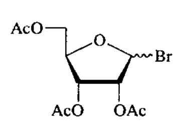
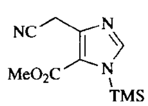
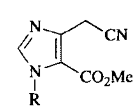
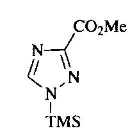
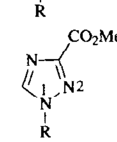
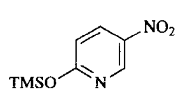
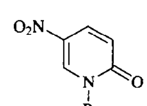
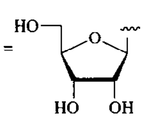
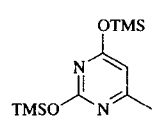
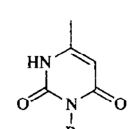
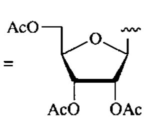
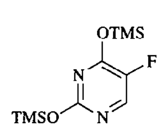
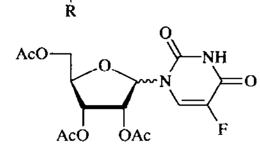
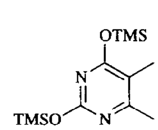
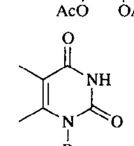
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Hg(CN)_2$, C_6H_6, reflux, 1 h	 (20) + N^7-isomer (12)	1131
		MeCN, reflux, 4 h	 I (51) R = 	691
		MeCN, reflux, 8 h	I (79)	691
		1. $Hg(CN)_2$, PhMe, 60-70°, 6 h 2. rt, 12 h	 (43)	1132
		MeCN, rt	 I (82)	728
		MeCN, reflux	I (46)	728
		1. MeCN, rt, 15 d 2. NH_3, MeOH, rt, 1 h	 (23) + N^3-isomer (15)	257
		1. $Hg(CN)_2$, PhMe, 60-70°, 6 h 2. rt, 12 h	 (37) R = 	1132
		MeCN, rt, 3 d	 (48) + N^3-isomer (6)	707
		MeCN, 25°, 3 d	 (51) + N^2-isomer (46)	259
		1. $Cl(CH_2)_2Cl$, reflux, 6 h; rt, 12 h 2. NH_3, MeOH, 0°, 4 d	 (72) R = 	714
		MeCN, rt, 3 d	 (16) R = 	89
		MeCN, rt, 16 h	 (50)	1133
		1. MeCN, rt, 3 d 2. NH_3, MeOH, rt, 12 h	 (17)	89

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

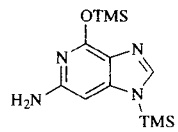
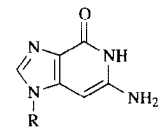
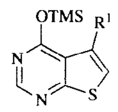
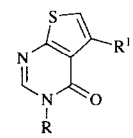
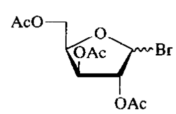
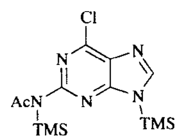
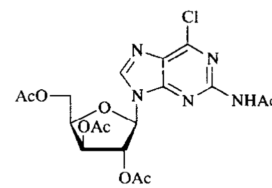
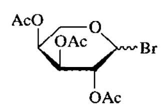
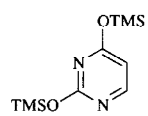
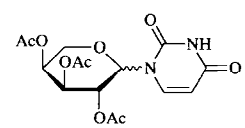
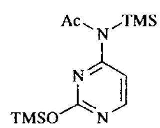
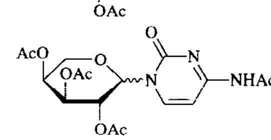
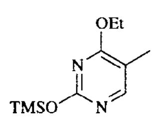
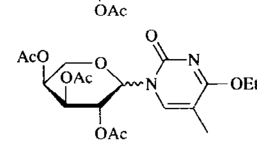
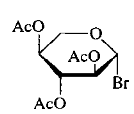
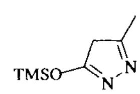
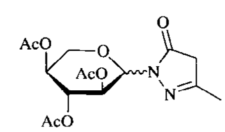
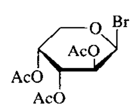
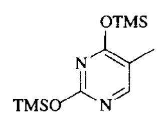
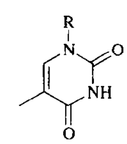
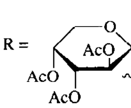
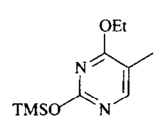
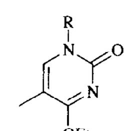
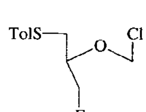
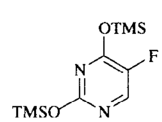
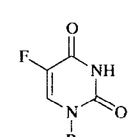
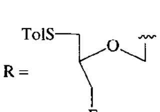
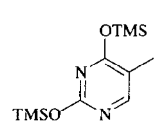
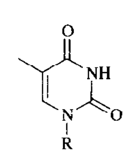
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. MeCN, rt, 3 d 2. NH_3, MeOH	 (55) N^7:N^9 = 1:8	705
		1. $HgBr_2$, HgO, C_6H_6, reflux, 20 h 2. NH_3, MeOH, rt, 20 h	 R^1: H (30); Me (40)	888
		$Hg(CN)_2$, C_6H_6, reflux, 17 h	 (62)	1134
		$Hg(OAc)_2$, HgO, or $AgClO_4$	 (90)	77
		$Hg(OAc)_2$, HgO, or $AgClO_4$	 (53)	77
		$Hg(OAc)_2$, HgO, or $AgClO_4$	 (53)	77
		$Hg(CN)_2$, $MeNO_2$, 80°, 5 h	 (6)	746
		$HgBr_2$, HgO, C_6H_6, 110°, 2 h	 (88) R = 	80
		$HgBr_2$, HgO, C_6H_6, 100°, 2-5 h	 (80)	80
		Bu_4NI, MeCN, reflux, 3 h, MeOH, 2 h	 **I** (96) R = 	1135
		$Hg(CN)_2$, C_6H_6, reflux, 3 h	**I** (97)	1135
		$Hg(CN)_2$, C_6H_6, reflux, 3 h, MeOH, 2 h	 (50)	1135

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

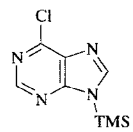
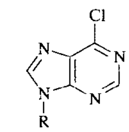
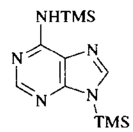
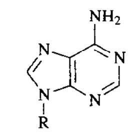
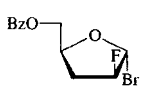
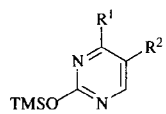
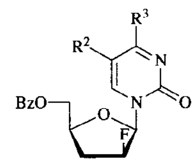
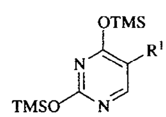
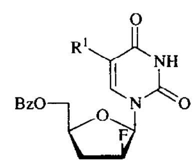
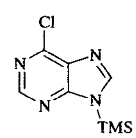
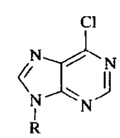
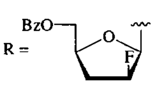
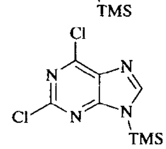
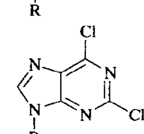
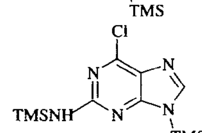
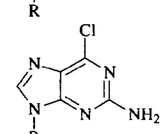
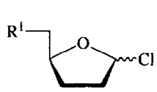
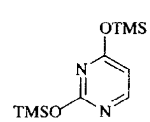
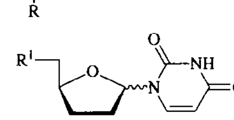
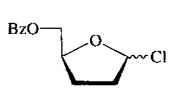
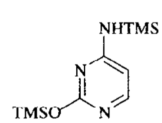
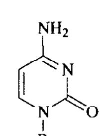
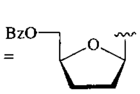
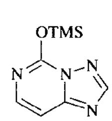
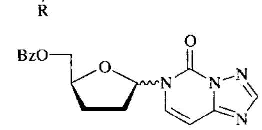
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		Bu_4NI, C_6H_6, reflux, 3 h	 (60)	1135
		$Hg(CN)_2$, MeCN, reflux, 3 h, MeOH, 2 h	 **I** (30)	1135
		Bu_4NI, C_6H_6, reflux, 3 h	**I** (20)	1131
C_{12} 		$Cl(CH_2)_2Cl$, reflux		
	R^1 / R^2		R^3	
	H / H	12 h	H (46)	389
	NHTMS / H	48 h	NH_2 (62) + α-anomer (6)	390
	NHTMS / F	4 h	NH_2 (66)	389
		$Cl(CH_2)_2Cl$, reflux, 48 h	 R^1: H (49), F (76), Cl (56), Me (50)	389
		MeCN, MS, rt, 14 h	 (41) + N^9-α-isomer (12); R = 	390
		$Hg(CN)_2$, MeCN, MS, reflux, 20 h	 (32) + α-anomer (23)	1136
		$Hg(CN)_2$, MeCN, reflux, 3 h	 (31) + N^7-isomer (7) + N^9-α-isomer (7)	1136
		Py, $CHCl_3$, rt, 12 h		
R^1				
p-$ClC_6H_4CO_2$			(85) α:β = 34:66	276
p-$O_2NC_6H_4CO_2$			(78) α:β = 39:61	276
		Py, $CHCl_3$, rt, 12 h	 (51) + α-anomer (25); R = 	276
		Py, $CHCl_3$, rt, 16 h	 (51) α:β = 44:56	957

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

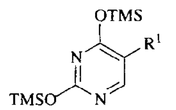
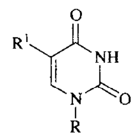
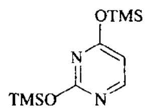
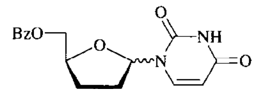
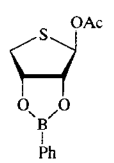
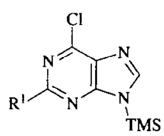
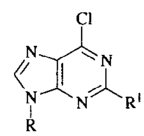
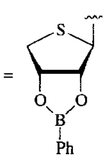
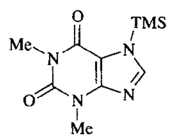
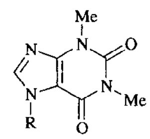
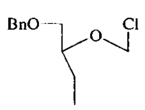
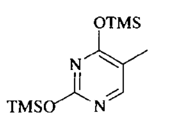
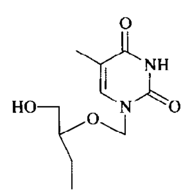
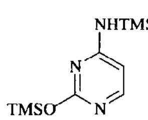
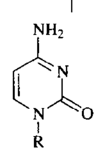
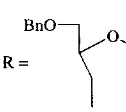
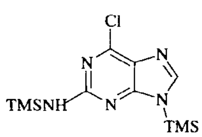
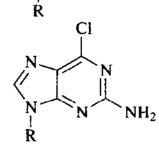
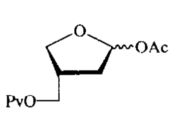
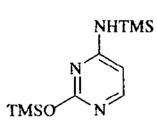
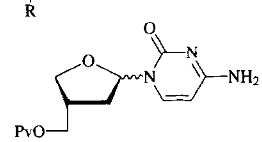
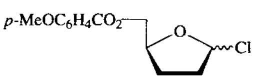
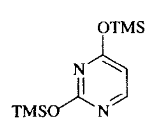
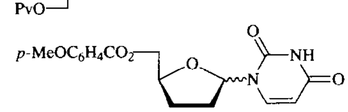
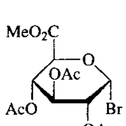
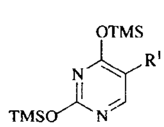
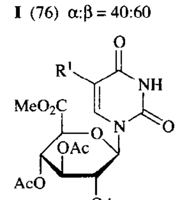
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		Py, $CHCl_3$, rt, 12 h	 R^1, α-anomer: H (53) (24); Me (52) (25)	276, 1137; 276
		$CHCl_3$, rt, 12 h	 I	276
		Py	I (77) α:β = 43:57	
		—	I (62) α:β = 42:58	
		$PhNMe_2$	I (73) α:β = 38:62	
		2-Picoline	I (70) α:β = 31:69	
		2,6-Lutidine	I (65) α:β = 32:68	
		Et_3N	I (58) α:β = 30:70	
		2,4,6-Collidine	I (49) α:β = 35:65	
		DMAP	I (37) α:β = 31:69	
		DBU	I (36) α:β = 33:67	
		TsOH, $MeNO_2$, rt, 12 h	 R^1: H (51); Cl (54); R = 	687
		TsOH, $MeNO_2$, rt, 12 h	 (31)	687
		1. MeCN, rt 2. H_2, cat.	 (82)	1122
		Bu_4NI, $Cl(CH_2)_2Cl$, reflux, 4.5 h	 (48) R = 	1138
		$Hg(CN)_2$, C_6H_6, reflux, 3 h	 (43)	1138
		TMSI, MeCN, 0°, 3 h	 (76) α:β = 1:1	139a
C_{13} 		Py, $CHCl_3$, rt, 12 h	 I (77) α:β = 31:69	276
		$CHCl_3$, rt, 12 h	I (76) α:β = 40:60	276
		$Hg(CN)_2$, $HgBr_2$, C_6H_6, reflux, 3.5 h	 R^1, bis(riboside): H (23) (4); F (38) (11); Cl (57) (—); Br (67) (11); I (72) (—)	767

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

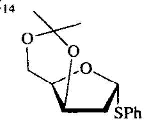
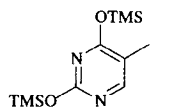
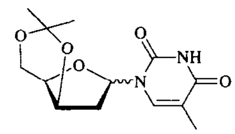
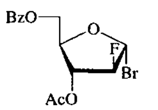
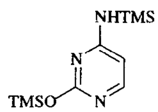
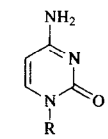
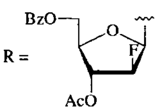
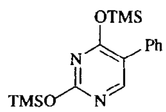
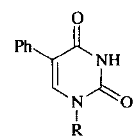
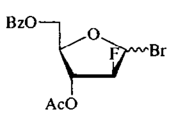
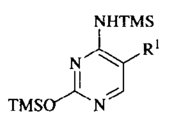
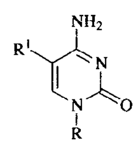
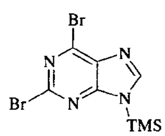
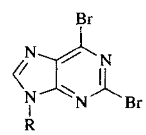
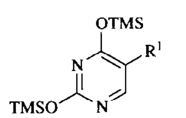
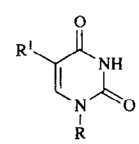
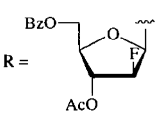
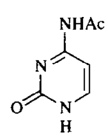
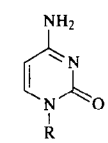
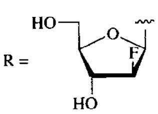
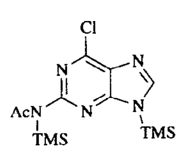
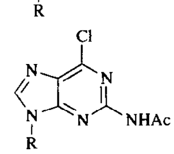
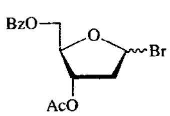
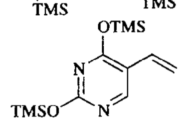
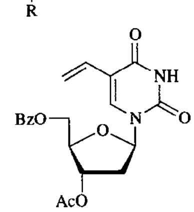
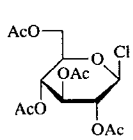
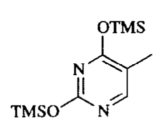
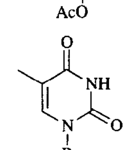
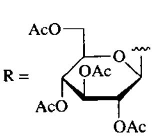
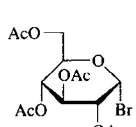
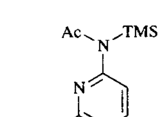
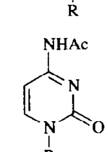
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 		NBS, CH_2Cl_2, MS, rt, 20 min	 (85) α:β = 1:30	405
		$CHCl_3$, reflux, 20 h	 (61) + α-anomer (21) R = 	386
		CH_2Cl_2, rt, 5 d	 (40)	1139
		CH_2Cl_2, rt, 7 d	 R^1: Me (57); I (32) + α-anomer (2)	1128
		$Cl(CH_2)_2Cl$, MS, 100°, 32 h	 (32)	1140
		C_6H_6, rt, 4 d	 R^1: CH_2=CHBr (26); Et (41) R = 	383
		1. CH_2Cl_2, 24°, 120 h 2. NH_3, MeOH, 10 h	 (41) R = 	1141
		$Hg(CN)_2$, C_6H_6, reflux, 4 h	 (32)	384
		CH_2Cl_2, rt, 7 d	 (43)	383
		HgO, $HgCl_2$, C_6H_6, 110°, 5 h	 (64) R = 	80
		HgO, $Hg(OAc)_2$, or $AgClO_4$	 (38)	77

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

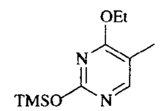
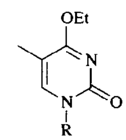
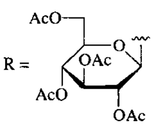
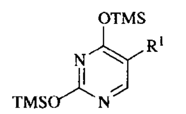
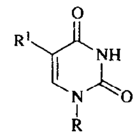
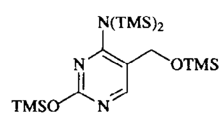
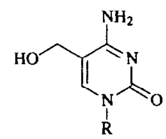
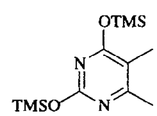
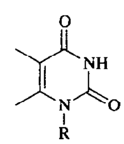
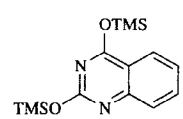
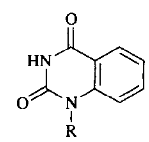
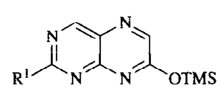
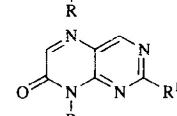
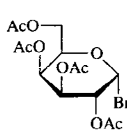
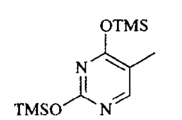
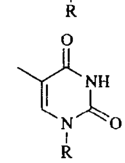
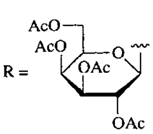
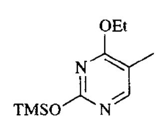
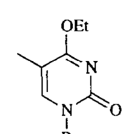
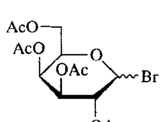
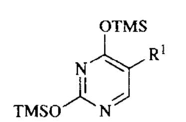
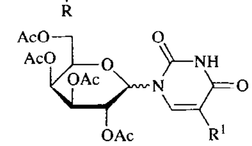
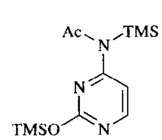
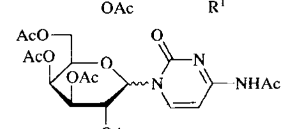
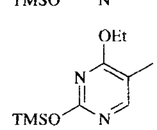
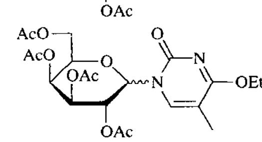
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		HgO, $HgBr_2$, C_6H_6, 100°, 2-5 h	 (81) R = 	80
				
	R^1			
	H	$HgBr_2$, C_6H_6, rt	(93)	1142
	H	HgO, $Hg(OAc)_2$, or $AgClO_4$	(44)	77
	Me	HgO, $HgCl_2$, C_6H_6, 110°, 5 h	(86)	80
	Me	HgO, $HgCl_2$, C_6H_6, 50°, 4 h	(72)	80
	Me	HgO, $Hg(OAc)_2$, or $AgClO_4$	(48)	77
	Me	C_6H_6, 100°, 20 h	(27)	80
		HgO, $Hg(OAc)_2$, or $AgClO_4$	 (79)	77
		HgO, $HgBr_2$, reflux	 (90)	1143
		HgO, $HgBr_2$, reflux	 (65)	1143
		HgO, $HgBr_2$, C_6H_6, reflux	 R^1: H, 5 h (8); NMe_2, 4 h (66)	1144
		HgO, $HgBr_2$, C_6H_6, 100°, 2 h	 (45) R = 	80
		HgO, $HgBr_2$, C_6H_6, 100°, 2-5 h	 (85)	80
		HgO, $Hg(OAc)_2$, or $AgClO_4$	 R^1: H (86); Me (50)	77
		HgO, $Hg(OAc)_2$, or $AgClO_4$	 (70)	77
		HgO, $Hg(OAc)_2$, or $AgClO_4$	 (91)	77

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

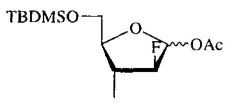
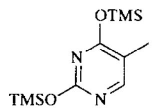
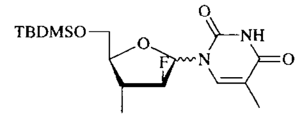
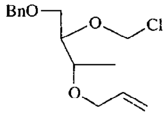
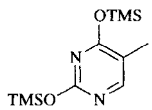
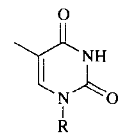
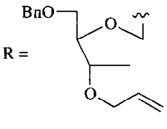
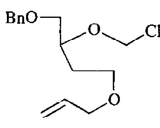
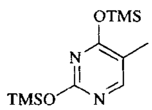
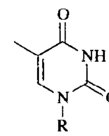
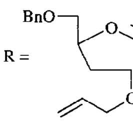
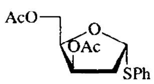
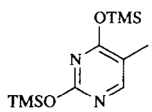
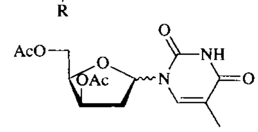
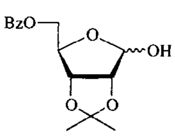
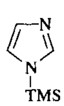
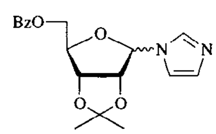
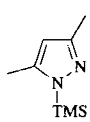
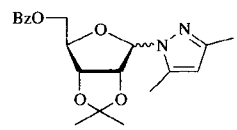
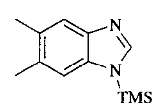
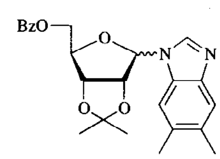
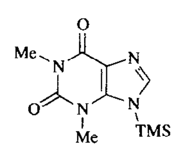
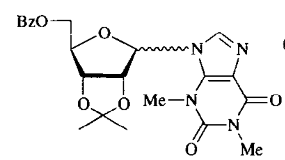
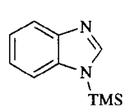
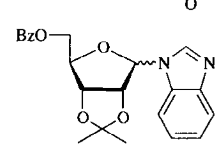
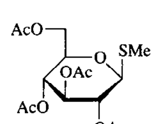
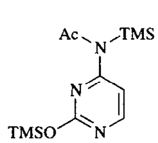
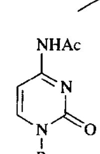
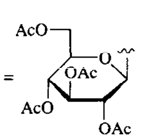
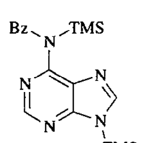
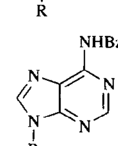
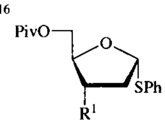
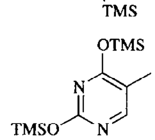
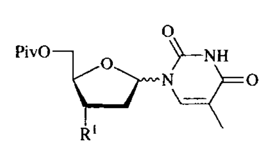
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		KI, dibenzo-18-crown-6, PhMe, MeCN, reflux, 4 h	 α-anomer (29) β-anomer (8)	392
C_{15} 		Bu_4NI, CH_2Cl_2, reflux, 12 h	 (88) R = 	1145
		Bu_4NI, CH_2Cl_2, reflux, 12 h	 (81) R = 	1145
		NBS, CH_2Cl_2, MS, rt, 20 min	 (93) α:β = 1:1.5	405
		1. FMPT 2. EtN(Pr-*i*)$_2$, CH_2Cl_2 –30°, 3 h, 0°, 1 d; rt, 1 d	 (82) α:β = 86:14	428
		1. FMPT 2. 1-ethylpiperidine, CH_2Cl_2, –30°, 3 h; 0°, 1 d; rt, 1 d	 (99) α:β = 84:16	428
		1. FMPT 2. 1-ethylpiperidine, CH_2Cl_2, –30°, 3 h; 0°, 1 d; rt, 1 d	 (80) α:β = 90:10	428
		1. FMPT 2. 1-ethylpiperidine, CH_2Cl_2, –30°, 3 h; 0°, 1 d; rt, 1 d	 (32) α:β = 53:47	428
		1. FMPT 2. EtN(Pr-*i*)$_2$, CH_2Cl_2 –30°, 3 h; 0°, 1 d; rt, 1 d	 (82) α:β = 89:11	428
		NIS, CF_3SO_3H, $Cl(CH_2)_2Cl$, rt, 1 h	 (83) R = 	408
		NIS, CF_3SO_3H, $Cl(CH_2)_2Cl$, rt, 2 h	 (79)	408
C_{16} 		NBS, CH_2Cl_2, MS, rt, 20-30 min	 R^1: F (96) α:β = 6:1; N_3 (100) α:β = 4:1	404

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

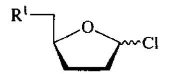
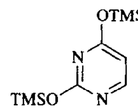
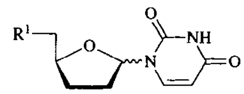
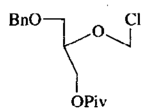
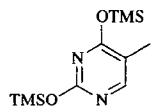
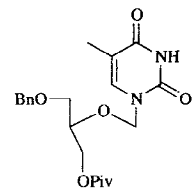
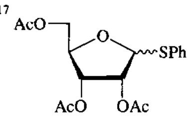
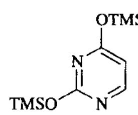
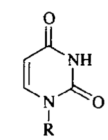
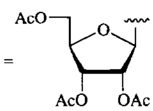
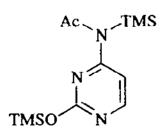
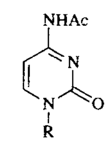
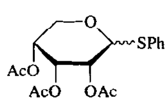
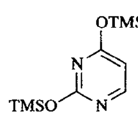
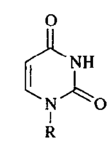
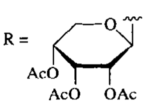
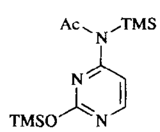
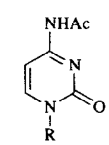
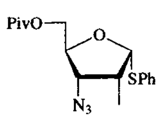
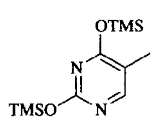
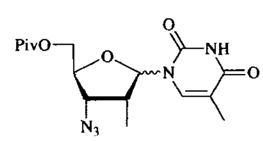
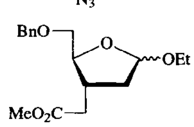
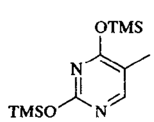
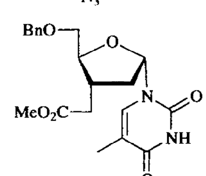
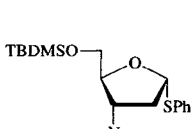
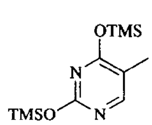
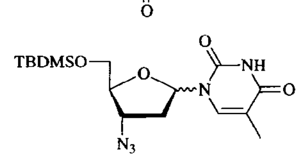
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
				276
R^1				
2-$C_{10}H_7CO_2$		Py, $CHCl_3$, rt, 12 h	(89) α:β = 33:67	
		$CHCl_3$, rt, 12 h	(94) α:β = 42:58	
1-$C_{10}H_7CO_2$		Py, $CHCl_3$, rt, 12 h	(51) α:β = 30:70	
		$CHCl_3$, rt, 12 h	(57) α:β = 40:60	
		Bu_4NI, $Cl(CH_2)_2Cl$, 50°, 1 h	 (40)	1146
C_{17} 		NIS, CF_3SO_3H, CH_2Cl_2, rt, 10 min	 (56) R = 	408
		NIS, CF_3SO_3H, CH_2Cl_2, rt, 45 min	 (81)	408
		NIS, CF_3SO_3H, CH_2Cl_2, rt	 (80) R = 	408
		NIS, CF_3SO_3H, CH_2Cl_2, rt, 30 min	 **I** (87)	408
		DMTST, MeCN, reflux, 30 min	**I** (83)	408
		NBS, CH_2Cl_2, MS, rt, 20-30 min	 (98) α:β = 9:1	404
		1. Me_2BBr, $CHCl_3$, –78 to 0° 2. $Cl(CH_2)_2Cl$, 0°	 (70) α:β = 1:3	278
		NBS, CH_2Cl_2, MS, rt, 20-30 min	 (100) α:β = 2:1	404

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

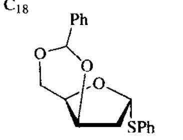
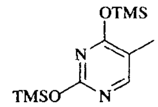
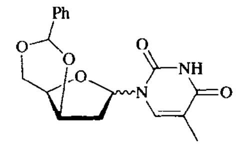
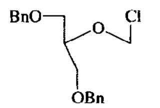
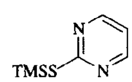
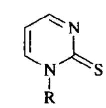
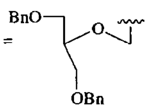
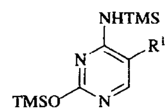
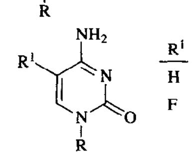
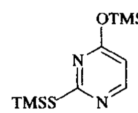
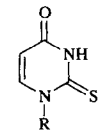
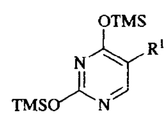
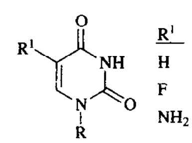
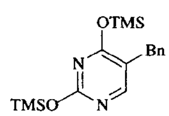
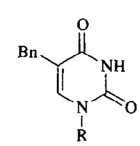
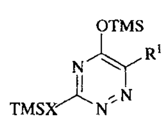
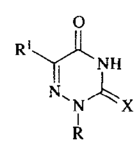
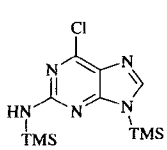
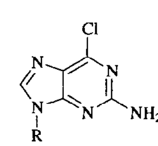
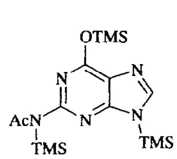
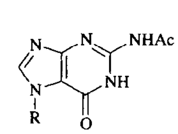
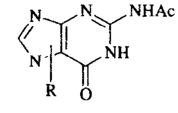
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 		NBS, CH_2Cl_2, MS, rt, 20 min	 (88) α:β = 1:12	405
		CsI, MeCN, reflux, 0.5 h	 (80) R = 	400
		Bu_4NI, $Cl(CH_2)_2Cl$, reflux, 45 min	 R^1: H (89); F (84)	786
		CsI, MeCN, reflux, 0.5 h	 I (95)	400, 1147
		$Hg(CN)_2$, C_6H_6, reflux, 3 h	I (23)	400, 1147
		CsI, MeCN, reflux, 1-2 h	 R^1: H (82); F (80); NH_2 (83)	400
		PhMe, reflux, 24 h	 (47)	1148
		MeCN		
	X = O, R^1 = Me	rt	(54) + N^1,N^3-bis(product) (10)	1122
	X = S, R^1 = Me	rt	(53)	1122
	X = O, R^1 = Ph	rt	(83)	1122
	X = O, R^1 = Bn	rt	(77)	1122
		Bu_4NI, MeCN, reflux, 2 h	 I (38)	788
		$Hg(CN)_2$, C_6H_6, reflux, 3 h	I (80)	788
		Bu_4NI, MeCN, reflux, 12 h	 I (28) + N^9-isomer (28)	788
		$Hg(CN)_2$, C_6H_6, reflux, 1.25 h	I (22) + N^9-isomer (14)	788
		$Cl(CH_2)_2Cl$, MS, reflux, 4 h	 (—) N^7:N^9 = 1:1	788

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

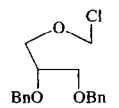
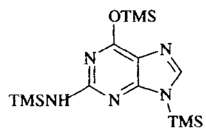
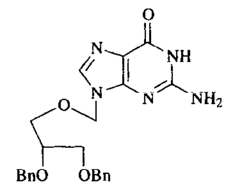
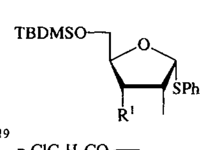
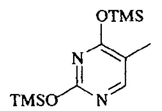
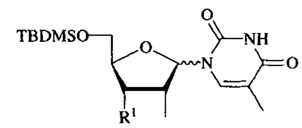
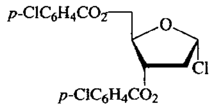
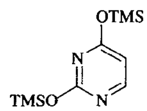
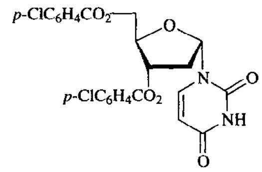
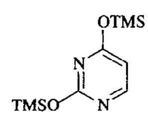
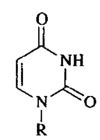
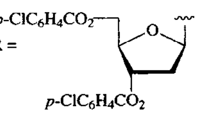
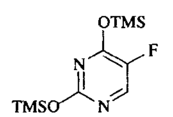
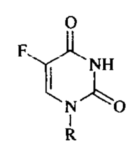
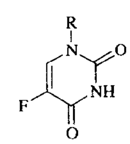
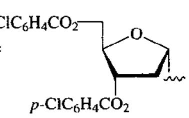
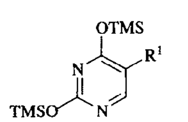
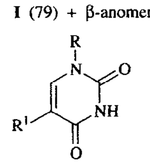
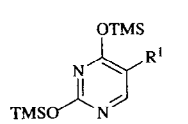
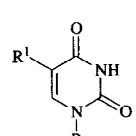
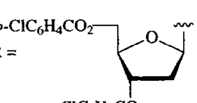
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. Xylene, 125°, 12 h 2. n-PrOH, AcOH, reflux, 1 h	 (50)	1149
		NBS, CH_2Cl_2, MS, rt, 20-30 min	 R^1 — αβ F (84) 3:1 N_3 (96) 4:1	404
C_{19} 		p-$O_2NC_6H_4OH$, Py, $CHCl_3$, 30°, 12 h	 (75) + β-anomer (21)	267
		p-$O_2NC_6H_4OH$, $CHCl_3$, 30°, 12 h	 (97) + α-anomer (2) R = 	267
		$CHCl_3$, rt, 24 h	 **I** (80)	1150
		p-$O_2NC_6H_4OH$, $CHCl_3$, 30°, 12 h	**I** (92) + α-anomer (5)	267
		KI, CH_2Cl_2, rt, 18 h	**I** (70)	1150
		CsF, CH_2Cl_2, rt, 20 h	**I** (—)	1151
		p-$O_2NC_6H_4OH$, $CHCl_3$, 25°, 12 h	 **I** R = 	267
		β-picoline	**I** (78)	
		α-picoline	**I** (77)	
		2,6-lutidine	**I** (62)	
		DMF	**I** (40)	
		Et_3N	**I** (73)	
		$AcNH_2$	**I** (51)	
		Py	**I** (79) + β-anomer (15)	
		p-$O_2NC_6H_4OH$, Py, $CHCl_3$, 30°, 12 h	 R^1 — β-anomer Cl (77) (10) Br (77) (21) I (82) (15) Me (67) (33)	267
	 R^1 Cl Br I Me	p-$O_2NC_6H_4OH$, $CHCl_3$, 30°, 12 h	 R =  — α-anomer (92) (5) (85) (10) (87) (9) (96) (—)	267

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

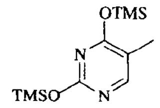
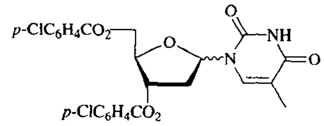
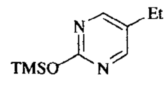
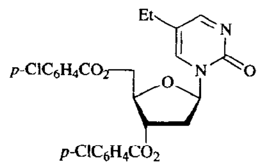
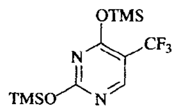
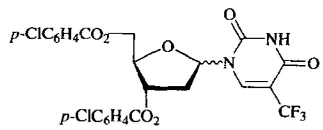
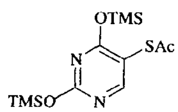
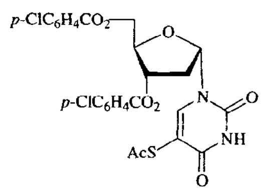
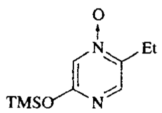
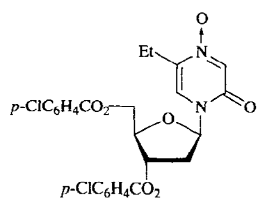
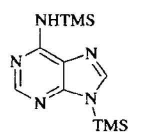
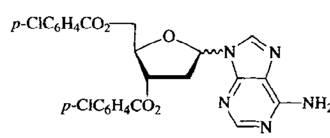
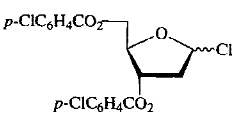
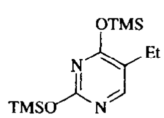
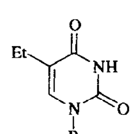
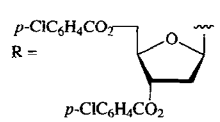
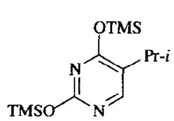
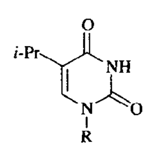
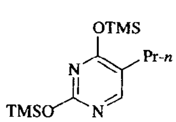
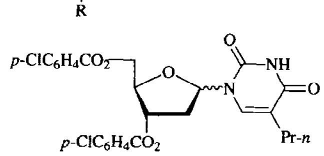
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 37°, 90 h	 (—) α:β = 1:1	266
		HgO, $HgBr_2$, PhMe, 0°, 35 min; rt, 2.5 h	 (16) + α-anomer (14)	1152
		$CHCl_3$, rt, 12-15 h		269
		p-$O_2NC_6H_4OH$	(77) α:β = 47:53	
		—	(82) α:β = 26:74	
		—, sugar:base = 1:8	(82) α:β = 26:74	
		—, sugar:base = 1:4	(78) α:β = 35:65	
		—, sugar:base = 1:2	(66) α:β = 44:56	
		C_6H_6, 37°, 90 h	 I (—)	266
		C_6H_6, reflux, 1.5 h	I (54) β-anomer only	266
		HgO, $HgBr_2$, $Cl(CH_2)_2Cl$, 0 - 5°, 30 min; rt, 15 min	 (44) + α-anomer (31)	621
		HMDS, 1,2,4-$Cl_3C_6H_3$, rt, 18 h	 (61) α:β = 43:57	790
		$Cl_2CHCHCl_2$, rt, 18 h	(58) α:β = 71:29	
		$CHCl_3$, rt, 18 h	(57) α:β = 55:45	
		1. $CHCl_3$, 10-15°, 2.5 h 2. MeOH	 (95) R = 	1153
		$CHCl_3$, rt, 30 min	 (90) + α-anomer (8)	1153
		$Hg(OAc)_2$, PhMe, rt, 24 h	 (82)	1154

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

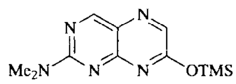
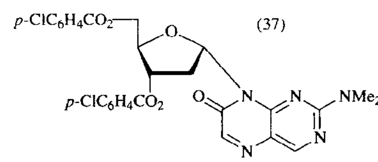
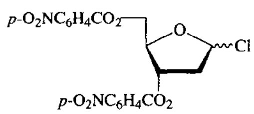
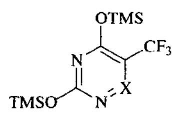
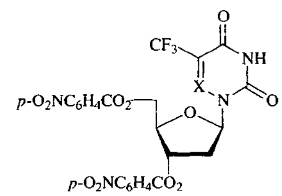
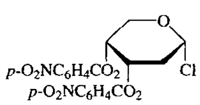
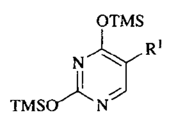
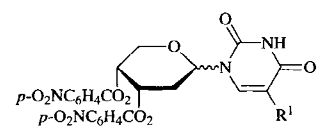
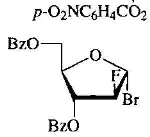
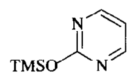
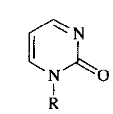
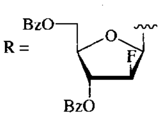
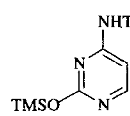
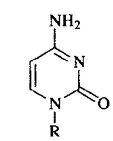
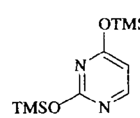
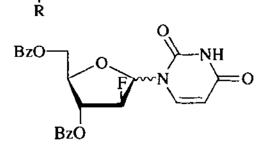
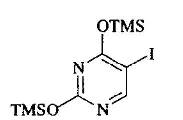
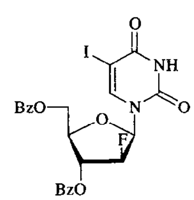
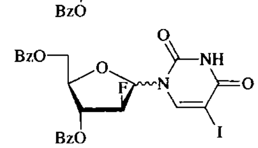
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		HgO, $HgBr_2$, C_6H_6, reflux, 5 h	 (37)	1144
		$Hg(OAc)_2$, C_6H_6		
	X			
	CH	25°, 18 h	(33) + α-anomer (23)	1155, 529
	N	rt, 3 d	(36)	1156
		$HgBr_2$, HgO	 R^1: H (80); Me (80)	997; 998
		$Cl(CH_2)_2Cl$, reflux, 18 h	 (65) R = 	388
		$CHCl_3$, reflux, 20 h	 (61)	386
		MeCN, reflux, 5 h	 I (—) α:β = 1:4	385
		CH_2Cl_2, reflux, 8.5 h	I (—) α:β = 1:8.5	385
		$CHCl_3$, reflux, 36 h	I (—) α:β = 1:20	385
		CCl_4, reflux, 60 h	I (—) α:β = 1:39	385
		NaI, CH_2Cl_2, MeCN, rt, 5 d	 (41)	1157
		NaI, MeCN, rt, 7 d	 I (96) α:β = 1:3	387
		MeCN, rt, 7 d	I (95) α:β = 1:7	387
		MeCN, reflux, 5 h	I (—) α:β = 1:2	385
		MeCN, reflux, 22 h	I (58) α:β = 1:9	387
		CH_2Cl_2, reflux, 44 h	I (—) α:β = 1:14	385
		$CHCl_3$, reflux, 36 h	I (—) α:β = 1:29	385
		CCl_4, reflux, 60 h	I (—) α:β = 1:34	385

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

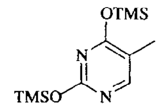
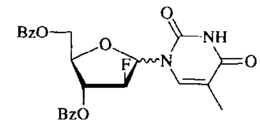
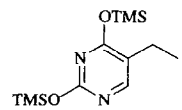
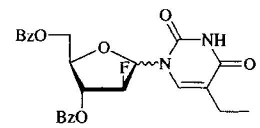
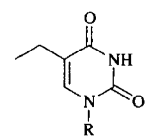
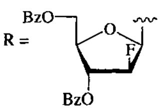
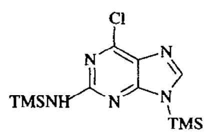
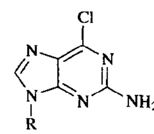
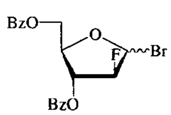
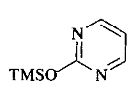
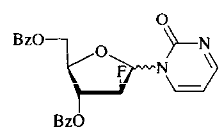
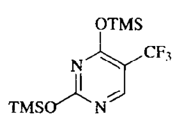
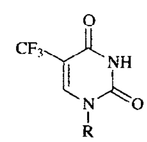
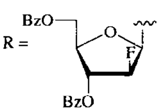
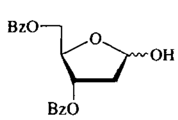
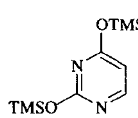
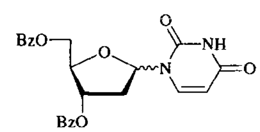
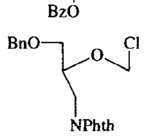
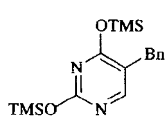
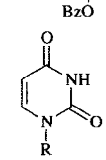
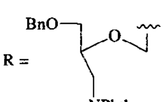
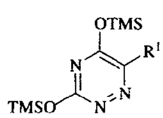
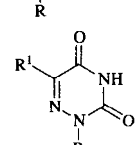
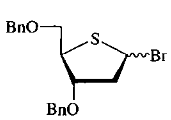
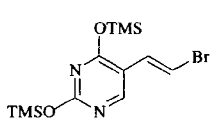
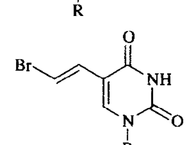
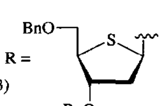
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, reflux, 1.5 h	 I (99) α:β = 1:4	387
		MeCN, reflux, 5 h	I (—) α:β = 1:3	385
		CH_2Cl_2, reflux, 44 h	I (—) α:β = 1:8.5	385
		$CHCl_3$, reflux, 36 h	I (—) α:β = 1:19	385
		CCl_4, reflux, 60 h	I (—) α:β = 1:36	385
		MeCN, reflux, 2 h	 I (63) α:β = 2:3	1158
		MeCN, reflux, 5 h	I (—) α:β = 1:2	385
		CH_2Cl_2, reflux, 44 h	I (—) α:β = 1:8.5	385
		$CHCl_3$, reflux, 36 h	I (—) α:β = 1:16	385
		CCl_4, reflux, 60 h	I (—) α:β = 1:41	385
		$CHCl_3$, reflux, 20 h	 (76) R = 	1158
		$Hg(CN)_2$, C_6H_6, reflux, 3 h	 (28) + α-anomer (6)	1136
		MeCN, reflux, 18 h	 (65)	1159
		$Hg(CN)_2$, rt, 18 h	 (80) R = 	383a
		$(TfO)_2O$, Py, CH_2Cl_2, reflux, 2 d	 (50)	1160
		PhMe, reflux, 24 h	 (58) R = 	1161, 1148
		MeCN, rt	 R^1: Ph (74); Bn (63)	1122
		CCl_4, 90-100°, 1 h	 (6) + α-anomer (3) R = 	1162

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

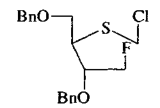
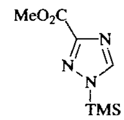
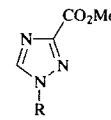
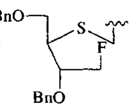
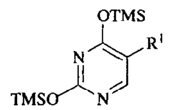
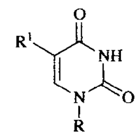
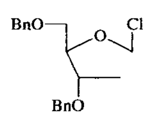
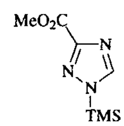
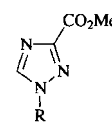
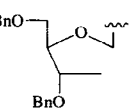
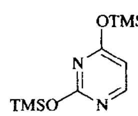
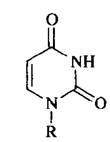
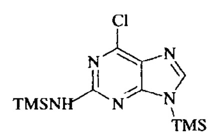
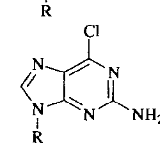
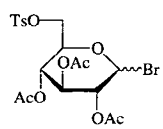
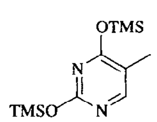
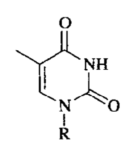
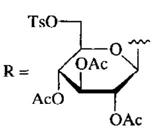
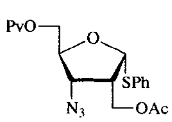
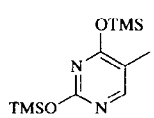
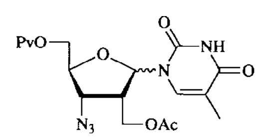
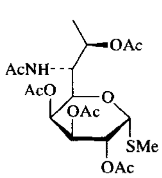
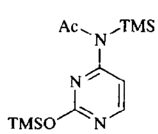
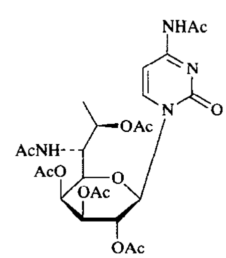
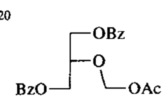
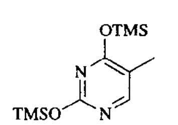
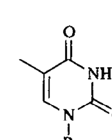
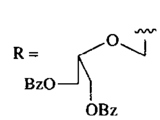
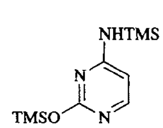
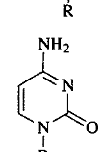
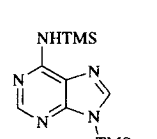
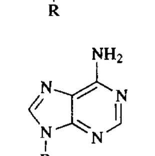
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		Bu_4NI, MeCN, reflux, 4.5 h; rt, 3 d	 (47) R = 	1163
		Bu_4NI, CH_2Cl_2, reflux	 R^1: H 4.5 h (99); Me 24 h (76)	1163
		Bu_4NI, MeCN, reflux, 4.5 h; rt, 3 d	 (64) R = 	1164, 751
		Et_4NI, CH_2Cl_2, reflux, 4.5 h	 (59) + N^3-anomer (7)	1165
		$Hg(CN)_2$, C_6H_6, reflux, 3 h	 (65) + N^7-anomer (5)	1165
		$HgCl_2$, HgO, C_6H_6, 60°, 4 h	 (63) R = 	753
		NBS, CH_2Cl_2, MS, rt, 20-30 min	 (81) α:β = 3:2	404
		NIS, CF_3SO_3H, $Cl(CH_2)_2Cl$, rt, 2 h	 (85)	408
C_{20} 		KI, dibenzo-18-crown-6, MeCN, C_6H_6, reflux, 2 d	 (80) R = 	1166
		KI, dibenzo-18-crown-6, MeCN, C_6H_6, reflux, 2 d	 (81)	1166
		KI, dibenzo-18-crown-6, MeCN, C_6H_6, reflux, 5 d	 (76)	1166

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

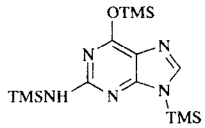
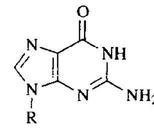
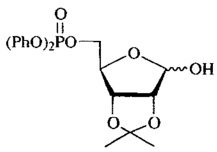
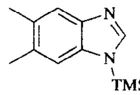
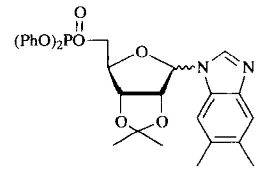
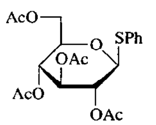
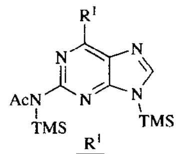
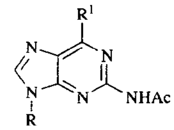
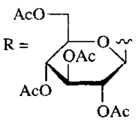
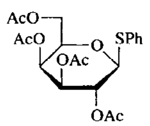
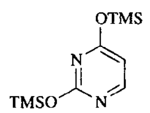
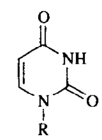
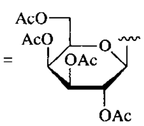
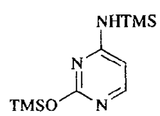
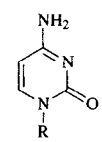
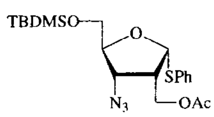
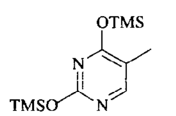
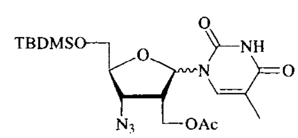
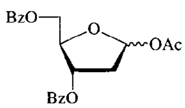
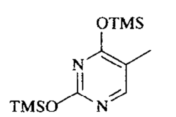
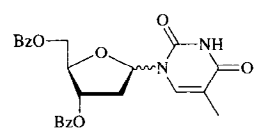
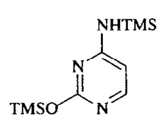
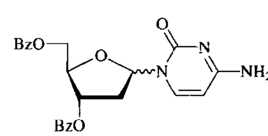
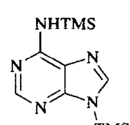
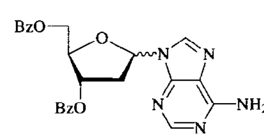
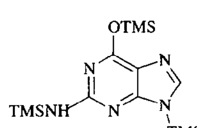
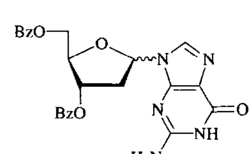
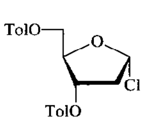
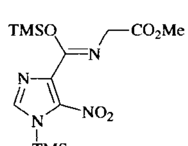
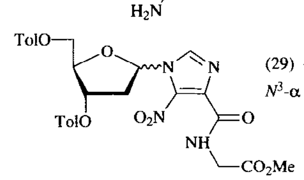
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		KI, dibenzo-18-crown-6, MeCN, C_6H_6, reflux, 1 d	 (80)	1166
		1. FMPT 2. $EtN(Pr\text{-}i)_2$	 (72) α:β = 89:11	433
	 R¹: H; Cl	NIS, $Cl(CH_2)_2Cl$, TfOH, rt, 3 h	 I R =  I (59) N^7:N^9 = 2:98; I (63) N^7:N^9 = 2:98	409
		NIS, CH_2Cl_2, TfOH, rt, 45 min	 (83) R = 	408
		NIS, CH_2Cl_2, TfOH, rt, 30 min	 (90)	408
		NBS,CH_2Cl_2, MS, rt, 20-30 min	 (72) α:β = 4:3	404
C_{21} 		KI, dibenzo-18-crown-6, MeCN:PhMe (1:1), reflux, 2-4 h	 (70)	396
		KI, dibenzo-18-crown-6, MeCN:PhMe (1:1), reflux, 2-4 h	 (77) α:β = 54:46	396
		KI, dibenzo-18-crown-6, MeCN:PhMe (1:1), reflux, 2-4 h	 (95) α:β = 62:38	396
		KI, dibenzo-18-crown-6, MeCN:PhMe (1:1), reflux, 2-4 h	 (90) α:β = 68:32	396
		Et_3N, $CHCl_3$, rt, 2 h	 (29) + N^3-α + β-isomers (18)	1167

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

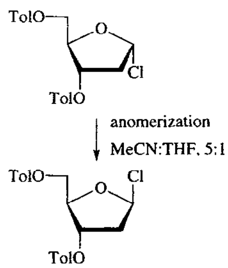
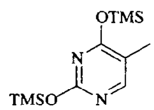
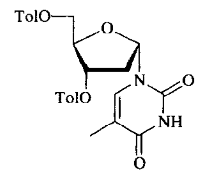
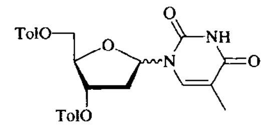
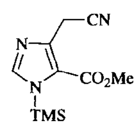
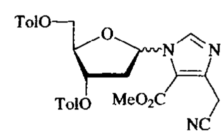
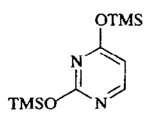
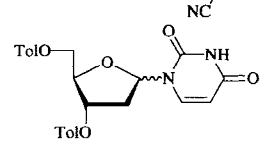
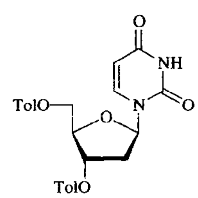
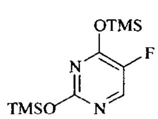
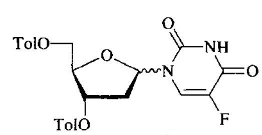
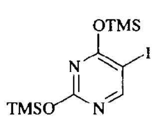
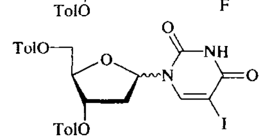
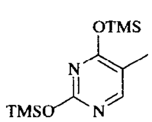
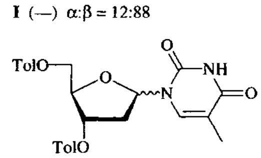
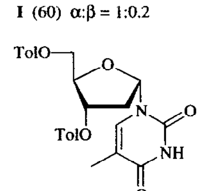
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, THF, 4°, 15 h	 (61) + β-anomer (19)	1168
		MeCN:THF (5:1), 4°, 18 h	 (—) α:β = 3:1	1169
		$Cl(CH_2)_2Cl$, rt, 72 h	 (36)	802a
		CuI, $CHCl_3$, rt, 2 h	 I (93) α:β = 8:92	273
		HgO, $HgBr_2$, C_6H_6, 20°, 10 h	I (38) + α-anomer (17)	80
		$CHCl_3$, rt, 24 h	 (92)	261
		CuI, $CHCl_3$, rt, 2 h	 (90) α:β = 27:73	273, 273a
		CuI, $CDCl_3$, rt, 20 h	 I (97) α:β = 12:88	273
		$CDCl_3$, rt, 20 h	I (97) α:β = 35:65	273
		CuI, $CDCl_3$, rt, 5 h	I (87) α:β = 10:90	273
		$CDCl_3$, rt, 5 h	I (77) α:β = 28:72	273
		CuI, $CHCl_3$	I (—) α:β = 12:88	273a
		CuI, $CHCl_3$, rt, 2 h	 I (92) α:β = 7:93	273, 273a
		MeCN, rt, 24 h[c]	I (60) α:β = 1:0.2	261
		MeCN, THF, 10°, 10 h	 I (61) + β-anomer (20)	802a
		$Hg(OAc)_2$, DMF, 20°, 48 h	I (27) + β-anomer (21)	80

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

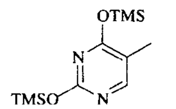
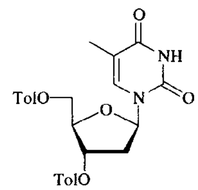
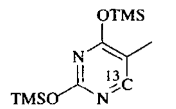
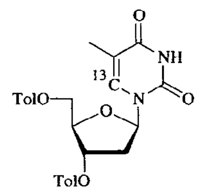
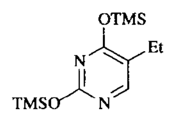
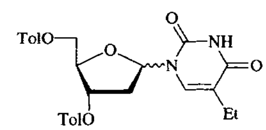
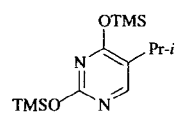
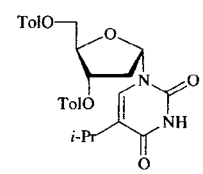
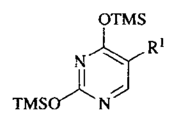
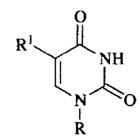
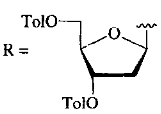
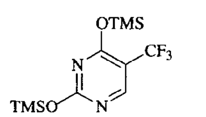
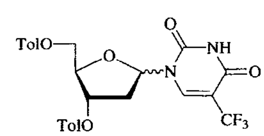
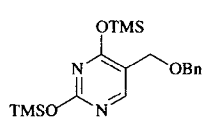
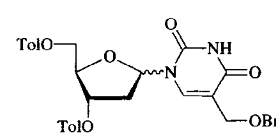
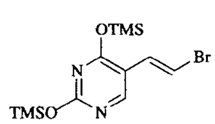
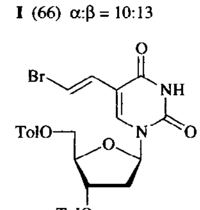
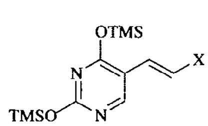
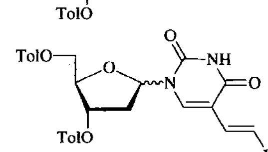
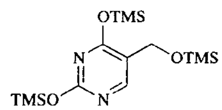
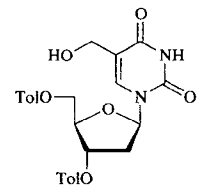
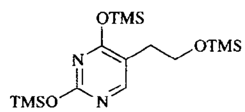
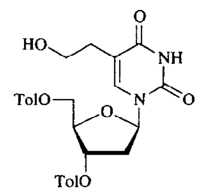
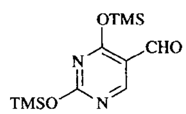
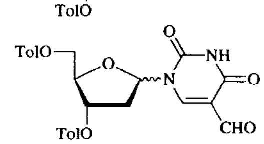
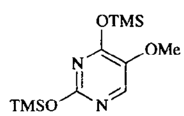
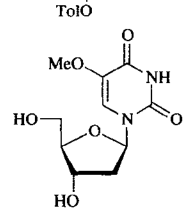
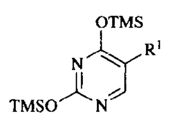
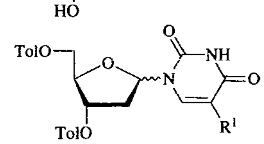
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$CHCl_3$, rt, 12-24 h	 (78-83)	261, 1170
		$CHCl_3$, rt, 12 h	 (73)	1150, 1171
		CuI, $CHCl_3$, rt, 2 h	 I (92) α:β = 7:93	273, 273a
		$Cl(CH_2)_2Cl$, MS, rt, 12 h	 (—)	289
			 R = 	
	R¹			
	Pr-*i*	$CHCl_3$, rt, 20-24 h	(95)	1172
	Bu-*t*	$CHCl_3$, rt, 20-24 h	(98)	1172
	C≡CH	$HgBr_2$, $Cl(CH_2)_2Cl$, 23°, 23 h	(67) α:β = 1:1.45	872
	c-C_3H_5	$CHCl_3$, rt, 20-24 h	(92)	1172
	C_5H_9	$CHCl_3$, rt, 20-24 h	(96)	1172
	C_6H_{11}	$CHCl_3$, rt, 20-24 h	(99)	1172
		$Hg(OAc)_2$, C_6H_6, rt, 18 h	 I (86) α:β = 1:2	1173
		$Hg(OAc)_2$, C_6H_6, 25°, 3 d	I (91) α:β = 1:2	529
		MeCN, MS, 25°, 2 d	 I (71) α:β = 19:10	1174
		C_6H_6, MS, 25°, 2 d	I (66) α:β = 10:13	1174
		$CHCl_3$, rt, 24 h	 (72)	261
		$Cl(CH_2)_2Cl$, 22°, 8 h	 X: Br (88) α:β 1.3:1; I (—) —	1175

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, MS, 25°, 2 d	 (10) + α-anomer (79)	1174
		$CHCl_3$, rt, 12 h	 (68)	1177a
		MeCN, MS, 25°, 2 d	 (31)	1174
		1. MeCN, rt, 64 h 2. NaOMe, MeOH, 6 h	 (31)	1178
				

R^1	Conditions	Product(s) and Yield(s) (%)	Refs.
NO_2	CuI, $CHCl_3$, rt, 5 h	(90) mainly β	273
2-furyl	MeCN, rt, 12 h	(—) α:β = 2:1	750
2-thienyl	$Cl(CH_2)_2Cl$, MS, rt, 12 h	(—) α:β = 1:1.68	750
3-methyl-2-thienyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
3-methyl-2-thienyl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(73) α:β = 4.4:1	275
3-*n*-hexyl-2-thienyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
3-*n*-hexyl-2-thienyl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(87) α:β = 1.6:1	275

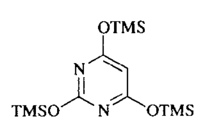
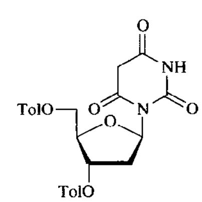
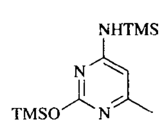
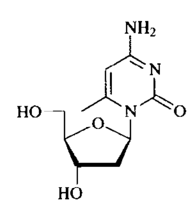
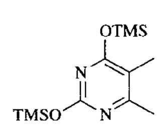
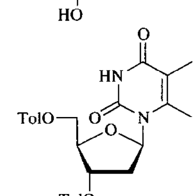
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$HgBr_2$, $Cl(CH_2)_2Cl$, rt, 1 h	 (31) + α-anomer (9)	364
		1. MeCN, MS, 20°, 4 d 2. NH_3, MeOH	 (14)	89
		CuI, $CHCl_3$, rt, 3 h	 (50)	274

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

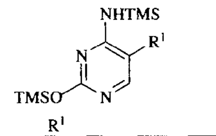
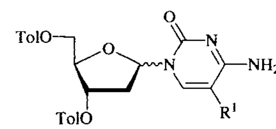
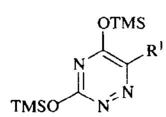
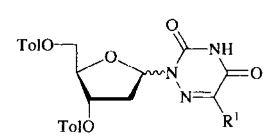
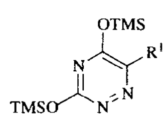
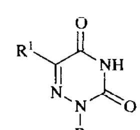
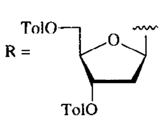
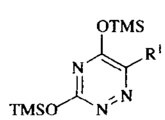
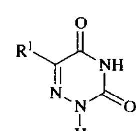
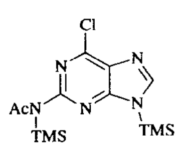
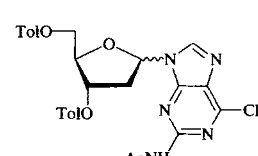
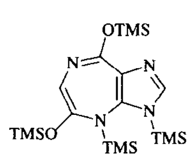
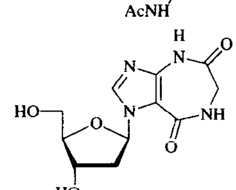
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
				
	R^1			
	c-C_3H_5	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	c-C_3H_5	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(77) $\alpha:\beta = 3.6:1$	275
	2-furyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	2-furyl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(75) $\alpha:\beta = 3.2:1$	275
	3-furyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	3-furyl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(76) $\alpha:\beta = 1:1.6$	275
	2-thiophenyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	2-thiophenyl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(79) $\alpha:\beta = 1:1.14$	275
	2-selenophenyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	2-selenophenyl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(68) $\alpha:\beta = 1.2:1$	275
	2-thiazolyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	2-thiazolyl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(69) $\alpha:\beta = 1:1.3$	275
	2-*N*-methylpyrryl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	2-*N*-methylpyrryl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(82) $\alpha:\beta = 1.4:1$	275
	2-(5-phenyl)-thiophenyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	2-(5-phenyl)-thiophenyl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(59) $\alpha:\beta = 1:1.14$	275
	Ph	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	Ph	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(49) $\alpha:\beta = 1:1.1$	275
	Ph	$HgBr_2$, MS, MeCN, rt, 10 d	(44) $\alpha:\beta = 4:1$	272
	2-pyridyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	2-pyridyl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(78) $\alpha:\beta = 1:1.88$	275
	3-pyridyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
	3-pyridyl	CuI, $Cl(CH_2)_2Cl$, rt, 12 h	(58) $\alpha:\beta = 2.4:1$	275
	4-pyridyl	$Cl(CH_2)_2Cl$, rt, 12 h	(—)	275
		CuI, $CHCl_3$, rt, 2 h	 R^1 / $\alpha:\beta$: H (92) 8:92; Me (92) 3:97	273, 273a
		CuI, $CHCl_3$, rt, 3 h	 R^1: H (70); Me (76); R = 	274
		$Hg(CN)_2$, C_6H_6, rt, 3 d	R^1 = H, (25)	1179
		$CHCl_3$, rt, 12 h	 R^1: c-C_3H_5 (81); 2-thienyl (94)	1180
		$Hg(CN)_2$, C_6H_6, reflux, 1.5 h	 (84) $\alpha:\beta = 1:1$	1134
		1. Et_3N, $CHCl_3$, 0°, 1 h, H_2O 2. NaOMe, rt, 2-3 h	 (41) + α-anomer (26)	1167

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

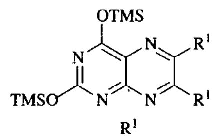
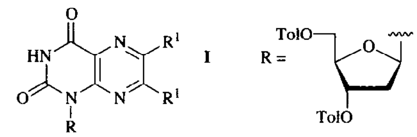
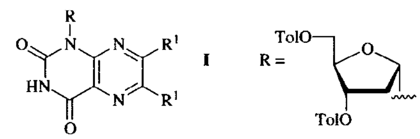
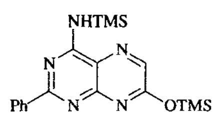
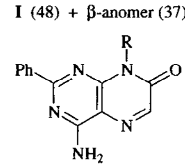
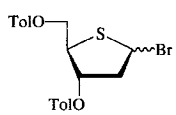
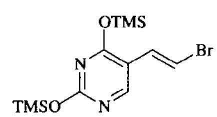
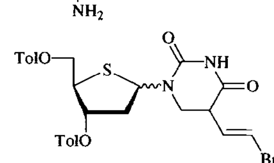
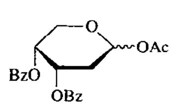
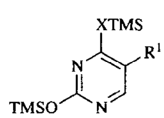
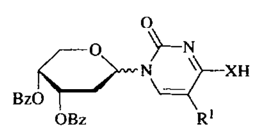
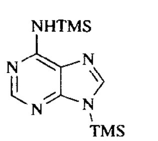
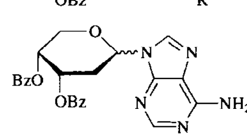
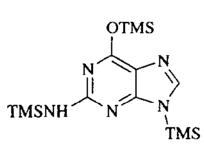
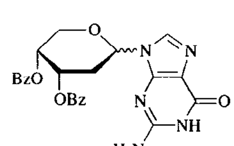
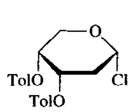
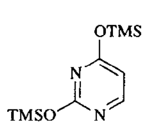
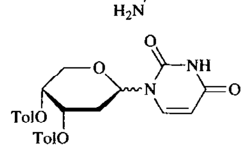
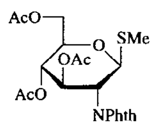
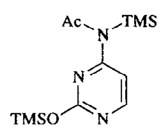
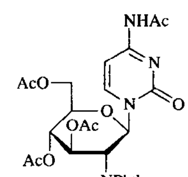
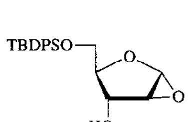
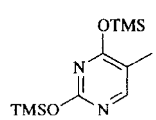
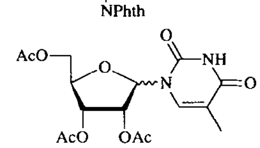
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
				
	R^1			
	H	CH_2Cl_2, 20°, 6 d	**I** (37) + α-anomer (37)	104
	H	CaI_2, $CHCl_3$, rt, 15 min	**I** (72) + α-anomer (7)	1029
	Me	C_6H_6, 20°, 7 d	**I** (43) + α-anomer (25)	104
	Ph	C_6H_6, 20°, 4 d	**I** (58) + α-anomer (22)	104
				
	R^1			
	H	HgO, $HgBr_2$, C_6H_6, reflux, 2 h	**I** (17) + β-anomer (5) + bis(riboside) (3)	905
	Me	"	**I** (23) + β-anomer (8) + N^1-α,β-isomers (2)	905
	Ph	"	**I** (29) + β-anomer (12)	905
	Ph	CH_2Cl_2, 20 °, 2 h	**I** (48) + β-anomer (37)	104
		HgO, $HgBr_2$, MS, C_6H_6, rt, 48 h	 (43)	1098
		CCl_4, 90-100°, 1 h	 (50) α:β = 1.8:1	1162
		KI, 18-crown-6, MeCN:PhMe (1:1), reflux, 2-4 h	 R^1 X α:β; H NH (71) 58:42; Me O (72) 60:40	396
		KI, 18-crown-6, MeCN:PhMe (1:1), reflux, 2-4 h	 (71) α:β = 44:56	396
		KI, 18-crown-6, MeCN:PhMe (1:1), reflux, 2-4 h	 (85) α:β = 58:42	396
		$HgBr_2$, HgO	 (78)	997
		NIS, $Cl(CH_2)_2Cl$, TfOH, rt, 1 h	 (70)	408
		1. MeCN, rt, 19.5 h 2. TBAF 3. Ac_2O, DMAP, rt, 12 h	 (36) α:β = 1:4	112

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

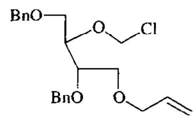
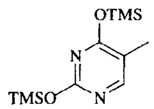
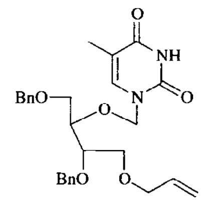
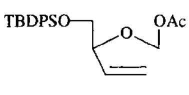
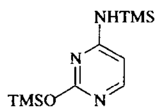
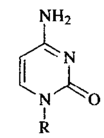
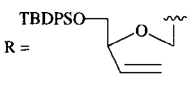
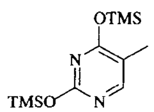
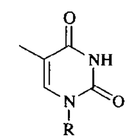
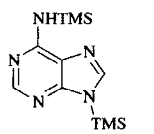
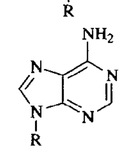
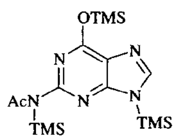
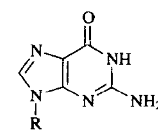
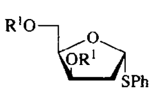
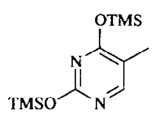
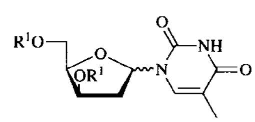
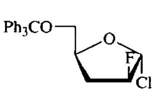
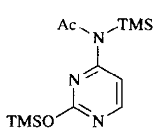
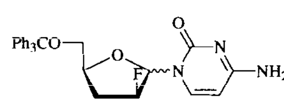
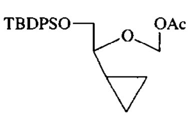
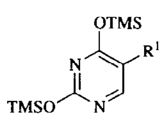
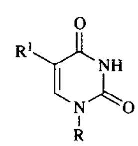
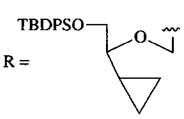
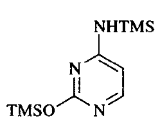
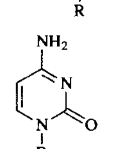
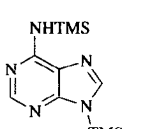
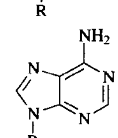
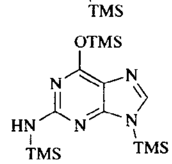
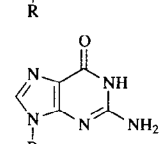
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		Bu_4NI, CH_2Cl_2, reflux, 12 h	 (99)	1145
C_{23}				
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 2-8 h	 (73) R = 	1181
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 2-8 h	 (90)	1181
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 2-8 h	 (65)	1181
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 2-8 h	 (98)	1181
 R^1 = TBDMS		NBS, CH_2Cl_2, MS, rt, 20 min	 (92) α:β = 1:5	405
C_{24}				
		1. $CHCl_3$, reflux, 12 h 2. MeOH, 20°, 30 min	 (—) α:β = 1:5	1182
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 2-8 h	 R^1: H (84), Me (90); R = 	397
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 2-8 h	 (78)	397
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 2-8 h	 (86)	397
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 2-8 h	 (61)	397

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

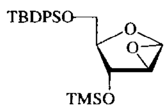
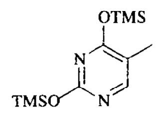
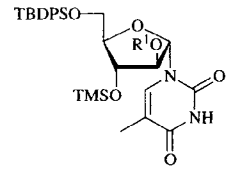
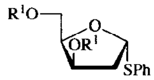
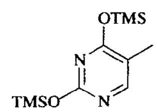
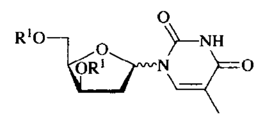
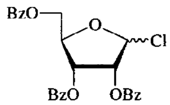
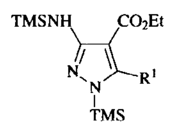
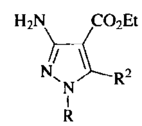
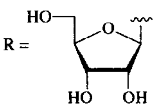
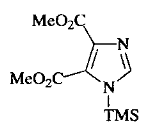
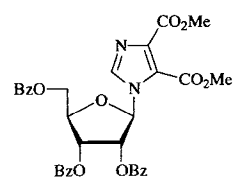
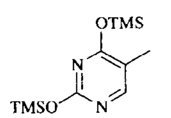
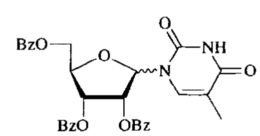
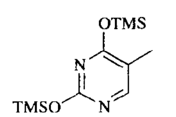
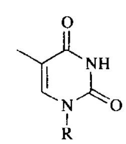
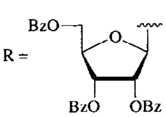
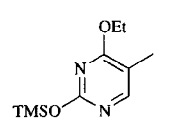
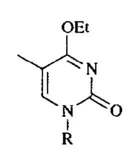
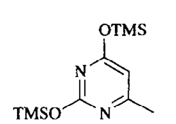
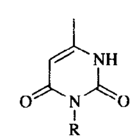
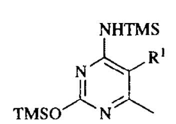
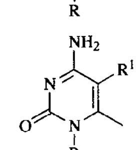
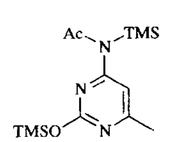
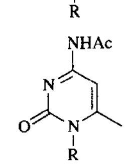
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, rt, 18 h	 R^1: TMS (52); H (30)	112
C_{25} 		NBS, CH_2Cl_2, MS, rt, 20 min	 R^1, α:β: Bz (86) 1:2; Bn (92) 1:4	405
C_{26} 		1. MeCN, rt, 5 d 2. NaOMe, MeOH	 I (22) R = 	1183
	R^1	Base:Sugar	R^2	
	H	4:5	H (22)	
	H	23.5:20	H (64)	
	NHTMS	4:5	NH_2 (60)	
	NHTMS	1:1	NH_2 (53)	
		$CHCl_3$, rt, 18 h	 (—)	853
		$Hg(OAc)_2$, C_6H_6, 20°, 60 h	 (65)	80
		HgO, $HgBr_2$, C_6H_6, 110°, 5 h	 I (80) R = 	80
		$Hg(OAc)_2$, C_6H_6, 20°, 60 h	I (65)	80
		HgO, $HgBr_2$, C_6H_6, 100°, 2-5 h	 (86)	80
		$Hg(OAc)_2$, MeCN, MS, reflux, 2 h	 (11) + bis(riboside) (33) + N^1-riboside (4)	60
		$Hg(OAc)_2$, MeCN, MS, reflux	 R^1: H 2 h (6); Me 3 h (8)	60
		$Hg(OAc)_2$, MeCN, MS, reflux, 4 h	 (4)	60

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

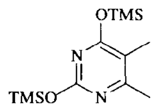
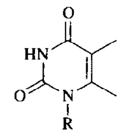
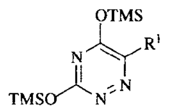
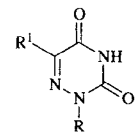
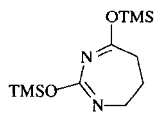
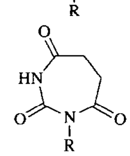
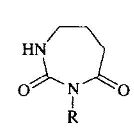
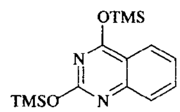
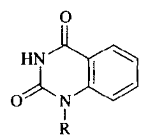
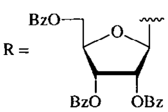
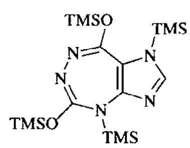
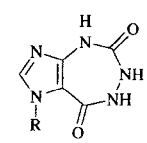
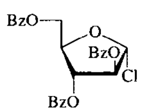
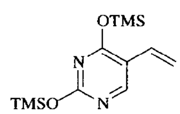
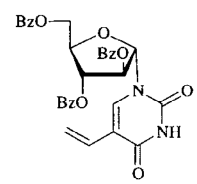
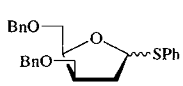
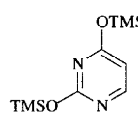
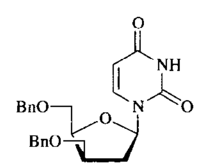
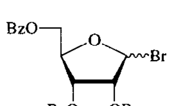
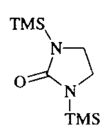
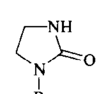
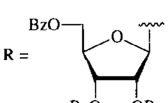
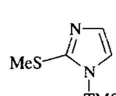
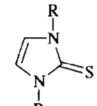
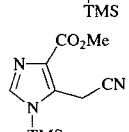
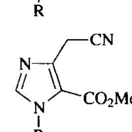
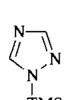
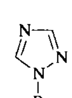
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		HgO, $HgBr_2$, C_6H_6, 100°, 7 h	 (42)	1143
		$Hg(OAc)_2$, PhMe, rt	 R[1]: Br (48); *N*-morpholinyl (50)	885
		HgO, $HgBr_2$, C_6H_6, reflux, 18 h	 (33) +  (21)	1184
		HgO, $HgBr_2$, C_6H_6, 100°, 7 h	 (84) R = 	1143
		$Hg(CN)_2$, PhMe, reflux, 2-3 h	 (39) + N^3-isomer (4)	507
		$Cl(CH_2)_2Cl$ or MeCN	 (—)	363
		NBS, CH_2Cl_2, rt, 20 min	 (72) α:β = 1:4	1185
		HgO, $HgBr_2$, C_6H_6, reflux, 18 h	 (49) R = 	511
		MeCN, rt, 4 d	 (50)	701
		MeCN, rt, 3 d	 (48) + N^3-isomer (6)	704, 707
		MeCN, rt, 4 d	 (54)	258

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

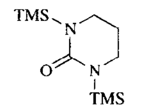
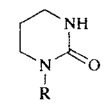
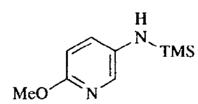
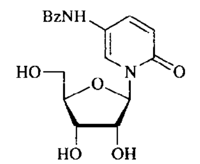
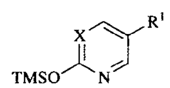
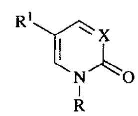
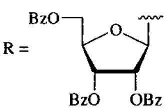
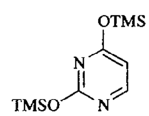
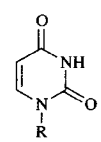
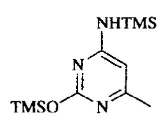
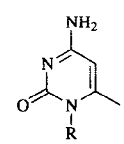
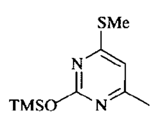
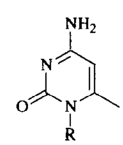
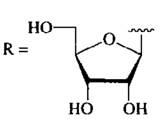
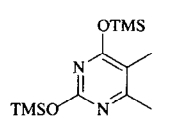
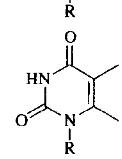
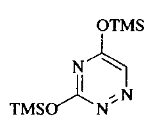
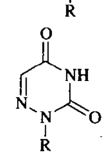
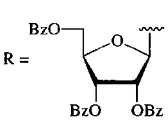
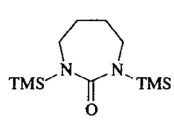
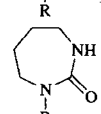
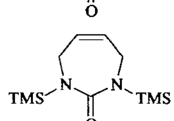
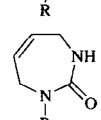
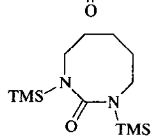
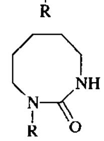
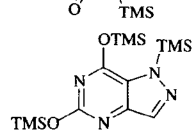
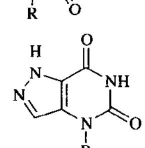
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		HgO, $HgBr_2$, C_6H_6, reflux, 18 h	 (76)	511
		1. MeCN, rt, 2.5 d 2. NH_3, MeOH	 (32)	1186
		MeCN	 R = 	
	X: CH, R^1: NO_2	rt, 2 d	(46)	1186
	X: CH, R^1: CO_2Me	rt, 3 d	(76)	1186
	X: N, R^1: H	reflux, 5 h	(27)	1187
		$HgBr_2$, rt	 (90)	1142
		MeCN, rt, 3 d	 (50)	89
		1. MeCN, rt, 3 d 2. NH_3, MeOH	 (8) R = 	89
		1. MeCN, rt, 3 d 2. NH_3, MeOH, rt, 12 h	 (11)	89
		$HgBr_2$	 (92) R = 	1142
		HgO, $HgBr_2$, C_6H_6, reflux, 18 h	 (46)	511
		HgO, $HgBr_2$, C_6H_6, reflux, 18 h	 (60)	511
		HgO, $HgBr_2$, C_6H_6, reflux, 18 h	 (42)	511
		MeCN, rt, 18 h	 (60)	362

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

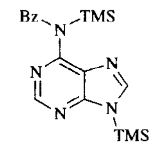
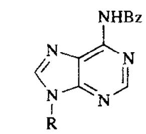
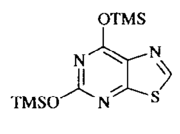
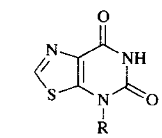
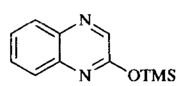
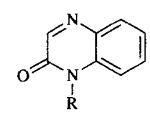
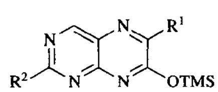
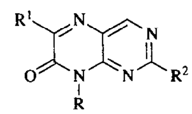
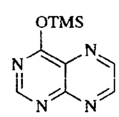
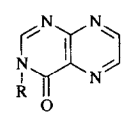
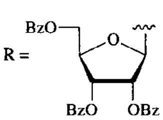
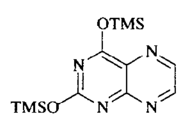
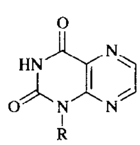
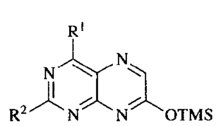
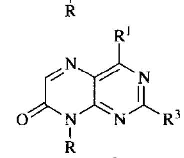
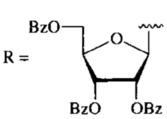
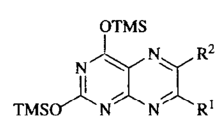
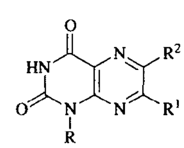
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$HgBr_2$, C_6H_6, rt, 3 h	 (40) + N^7-isomer (30)	1142
		DMF, rt, 3 d	 (46) + α-anomer (19)	901
		HgO, $HgBr_2$, C_6H_6, reflux, 8 h	 (8)	903
		HgO, $HgBr_2$, C_6H_6, reflux		1144
	R^1 / R^2			
	H / H	5 h	(41)	
	H / Me_2N	5 h	(49)	
	Me / Me_2N	3 h	(77)	
		HgO, $HgBr_2$, C_6H_6, reflux, 4 h	 (69) R = 	1188
		HgO, $HgBr_2$, C_6H_6, reflux, 4 h	 (50) + bis(riboside) (3)	905
		HgO, $HgBr_2$, C_6H_6,	 R = 	1144
	R^1 / R^2		R^3	
	NMe_2 / NHTMS	reflux, 10 h	NH_2 (36)	
	H / NMe_2	80°, 5 h	NMe_2 (49)	
				104
	R^1 / R^2			
	H / Ph	HgO, $HgBr_2$, C_6H_6, 80°, 4 h	(6) + N^1,N^3-bis(riboside) (22)	104
	H / Ph	CH_2Cl_2, 20°, 3 d	(19) + α-anomer (17)	104
	Ph / H	HgO, $HgBr_2$, C_6H_6, 80°, 4 h	(47) + N^1,N^3-bis(riboside) (12)	104
	Ph / H	CH_2Cl_2, 20°, 3 d	(52) + α-anomer (9)	104
	H / p-ClC_6H_4	CH_2Cl_2, 20°, 5 d	(21)	104
	p-ClC_6H_4 / H	CH_2Cl_2, 20°, 4 d	(46)	104
	Me / Me	HgO, $HgBr_2$, C_6H_6, 80°, 4 h	(44) + bis(riboside) (3)	905
	Ph / Ph	HgO, $HgBr_2$, C_6H_6, 80°, 4 h	(74) + N^3-β-isomer (5) + N^1,N^3-bis(riboside) (5)	104, 905
	p-ClC_6H_4 / p-ClC_6H_4	CH_2Cl_2, 20°, 4 d	(51) + α-anomer (7)	104

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

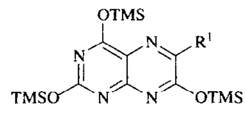
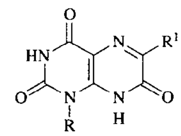
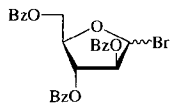
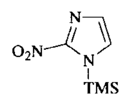
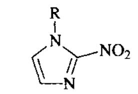
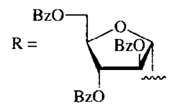
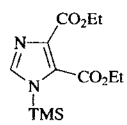
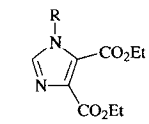
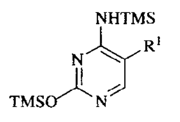
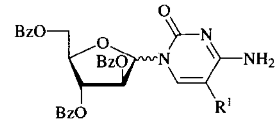
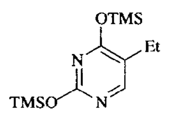
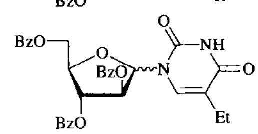
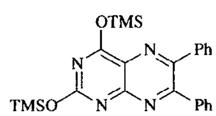
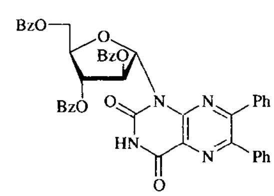
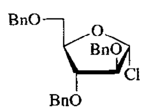
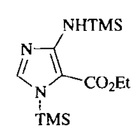
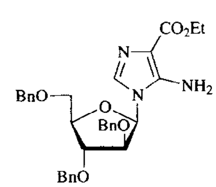
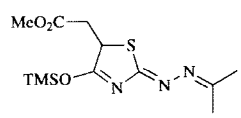
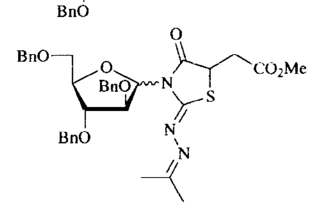
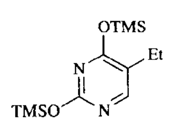
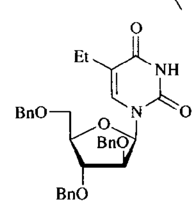
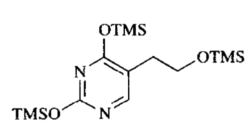
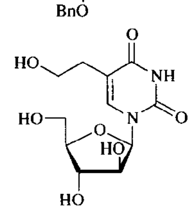
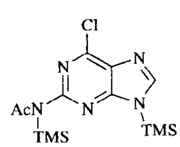
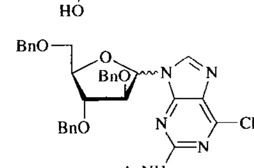
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		HgO, $HgBr_2$, C_6H_6, reflux, 4 h	 R^1: H (46); Me (34); Ph (18)	904
		$Hg(CN)_2$, MeCN, rt, 2 d	 (33) + β-anomer (7) R = 	760
		PhMe, reflux, 5 h	 (68) + β-anomer (7)	852
		PhMe, reflux, 2 h	 R^1: H (—); F (—)	499
		$Cl(CH_2)_2Cl$, MS, rt, 24 h	 (71) α:β = 5:2	358
		HgO, $HgBr_2$, C_6H_6, reflux, 4.5 h	 (45)	917
		MeCN, reflux, 1 h	 (15)	352
		CH_2Cl_2, MS, rt, 12 h	 (—) α:β = 2:1	839
		$Cl(CH_2)_2Cl$, MS, rt, 24 h	 (75)	358
		1. CH_2Cl_2, xylene, MS, rt, 2 d 2. H_2, Pd/C, EtOH	 (58)	360
		$Hg(CN)_2$, C_6H_6, reflux, 16 h	 (91)	1134

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

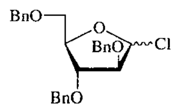
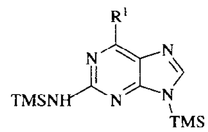
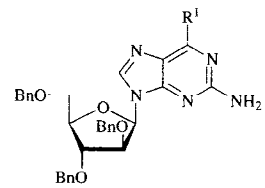
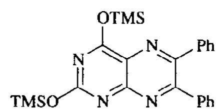
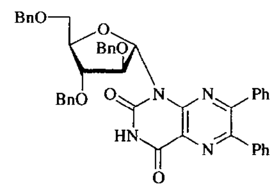
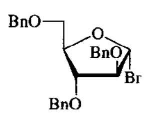
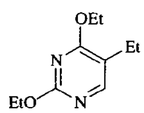
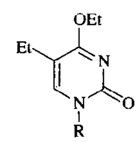
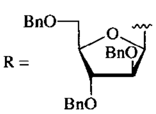
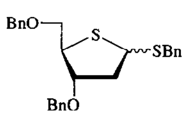
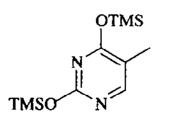
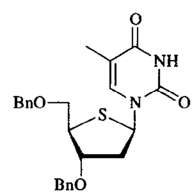
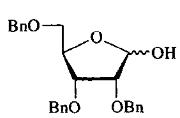
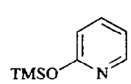
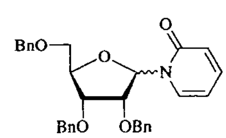
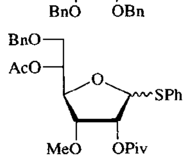
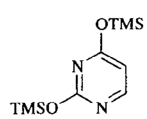
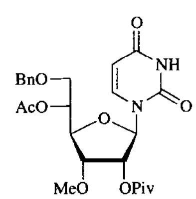
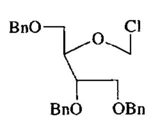
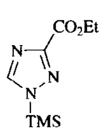
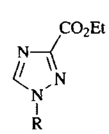
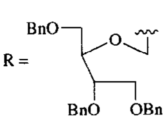
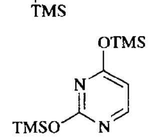
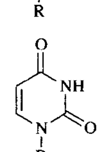
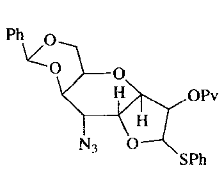
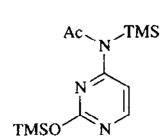
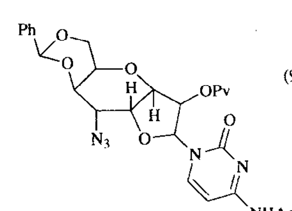
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
				
	R^1			
	Cl	$Cl(CH_2)_2Cl$, MS, rt, 5 d	(33)	1189
	NHTMS	1. $Cl(CH_2)_2Cl$, reflux, 18 h 2. MeOH, reflux, 15-30 min	(65)	346
		HgO, $HgBr_2$, C_6H_6, reflux, 4.5 h	 (29) + β-N^1-isomer (5) + N^1,N^3-α,α-bis(riboside) (34)	917
		MeCN, MS, rt, 5 d	 (49) R = 	358
		$HgBr_2$, $CdCO_3$, PhMe, reflux, 24 h	 (8) + α-anomer (28)	1162
		1. FMPT 2. 1-ethylpiperidine, CH_2Cl_2, –30°, 3 h; 0°, 1 d; rt, 1 d	 (71) α:β = 76:24	428
		NIS, TfOH, CH_2Cl_2, –20 to 0°	 (85)	410
		Et_4NI, MeCN, reflux, 4.5 h, rt, 3 d	 (33) R = 	1164
		Et_4NI, MeCN, reflux, 9 h, rt, 15 h	 (62)	1165
		NIS, TfOH, CH_2Cl_2, 23°, 1 h	 (95)	408a

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

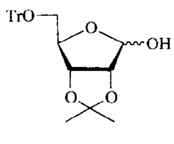
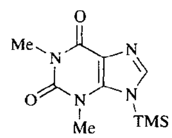
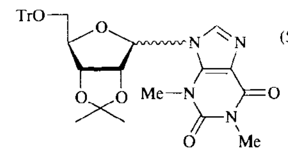
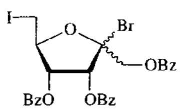
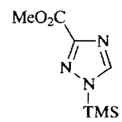
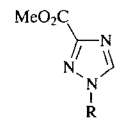
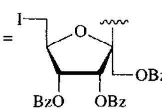
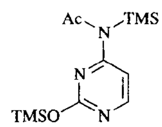
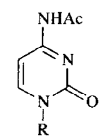
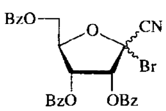
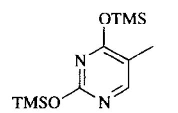
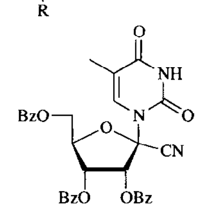
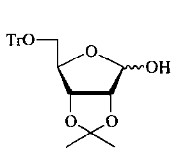
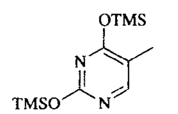
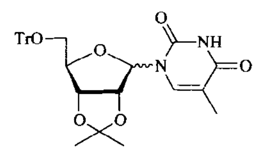
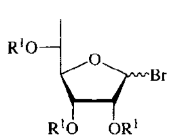
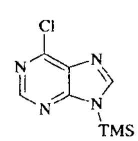
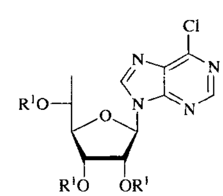
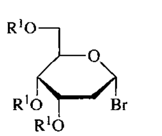
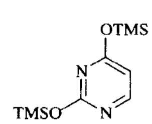
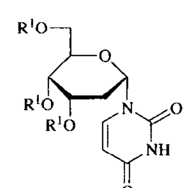
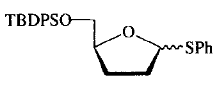
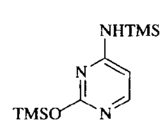
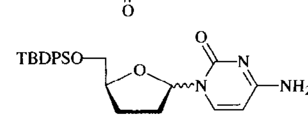
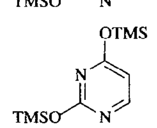
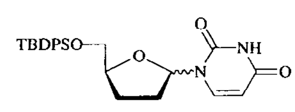
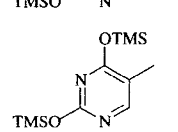
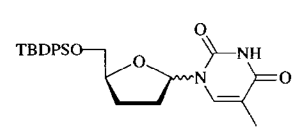
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27} 		1. FMPT 2. 1-ethylpiperidine, CH_2Cl_2, –30°, 3 h; 0°, 1 d; rt, 1 d	 (53) α:β = 32:68	428
		$Hg(CN)_2$, C_6H_6, 60°, 2.5 h	 (49) R = 	632
		$Hg(CN)_2$, C_6H_6, 60°, 19 h	 (20)	632
		$Hg(CN)_2$, $MeNO_2$, rt, 3 d	 (56)	1190
		1. FMPT 2. 1-ethylpiperidine, CH_2Cl_2, –30°, 3 h; 0°, 1 d; rt, 1 d	 (71) α:β = 76:24	428
 R^1 = p-$O_2NC_6H_4CO$		$HgBr_2$, $Hg(CN)_2$, $Cl(CH_2)_2Cl$, MS, rt, 12 h	 (91)	844
 R^1 = p-$O_2NC_6H_4CO$		MeCN, $Cl(CH_2)_2Cl$, rt, 2 h	 (57)	1065
		NBS, CH_2Cl_2, MS, –78°, 135 min	 (79) α:β = 1:3	406
		NBS, CH_2Cl_2, MS, –78°, 135 min	 (87) α:β = 1:5.3	406
		NBS, CH_2Cl_2, MS[d]		
		–78° to rt, 2 h	(83) α:β = 1:3.6	406
		–30°, 135 min	(93) α:β = 1:3	406
		–0°, 135 min	(93) α:β = 1:2.6	406
		rt, 5 min	(94) α:β = 1:1.6	406

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

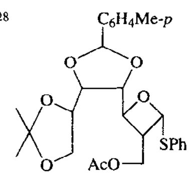
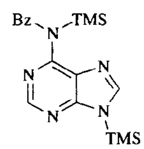
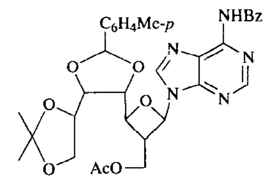
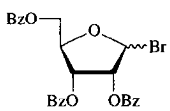
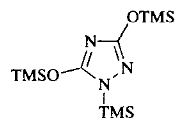
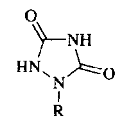
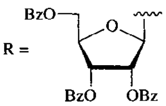
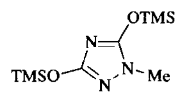
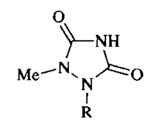
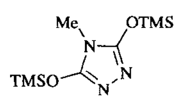
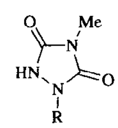
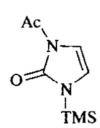
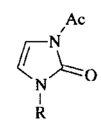
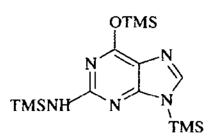
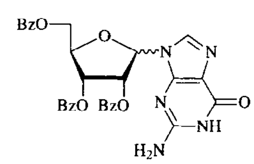
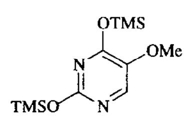
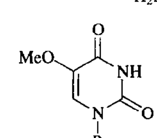
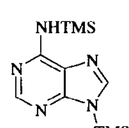
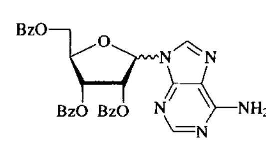
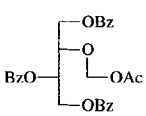
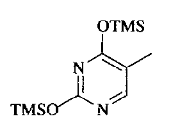
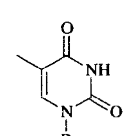
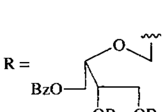
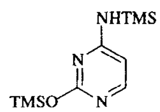
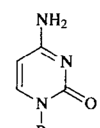
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28} 		NBS, CH_2Cl_2, MS, rt, 30 min	 (58)	403
		MeCN, rt, 3 d	 (84) R = 	258
		MeCN, 110°, 15 min	 (77)	258
		MeCN, rt, 3 d	 (46)	258
		$SnCl_4$, MeCN, 20°, 6 h	 (51)	777
		KI, 18-crown-6, MeCN:PhMe (1:1), reflux, 2-4 h	 (61) α:β = 24:76	396
		MeCN, rt, 48 h	 (75)	1178
		KI, 18-crown-6, MeCN:PhMe (1:1), reflux, 2-4 h	 (70) α:β = 32:68	396
		KI, dibenzo-18-crown-6, MeCN, C_6H_6, reflux, 3 d	 (87) R = 	1166
		KI, dibenzo-18-crown-6, MeCN, C_6H_6, reflux, 5 d	 (87)	1166

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

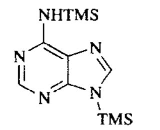
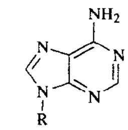
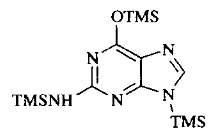
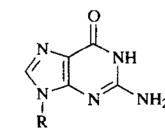
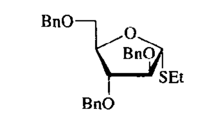
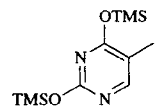
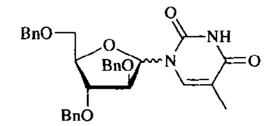
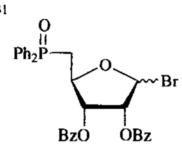
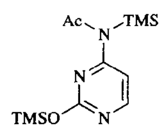
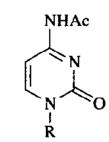
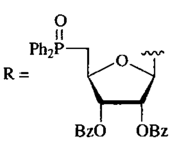
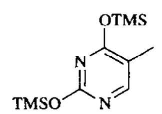
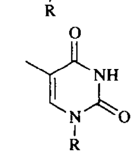
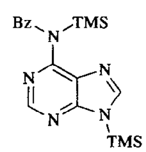
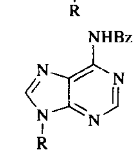
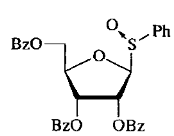
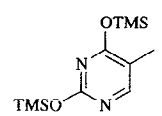
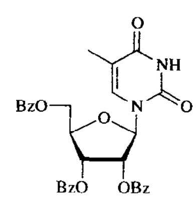
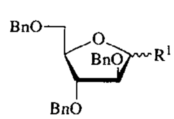
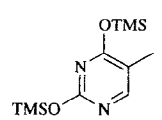
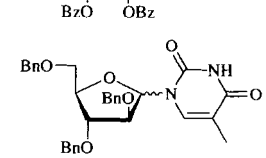
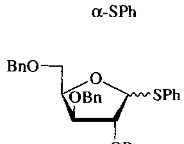
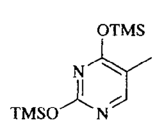
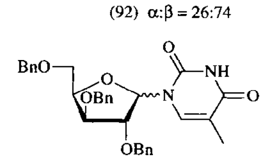
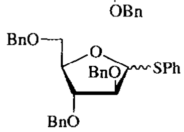
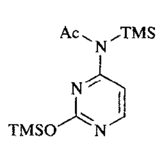
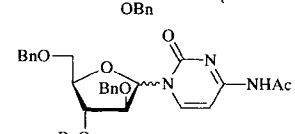
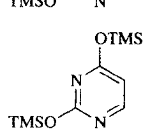
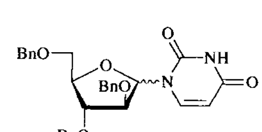
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		KI, dibenzo-18-crown-6, MeCN, C_6H_6, reflux, 4 d	 (78)	1166
		KI, dibenzo-18-crown-6, MeCN, C_6H_6, reflux, 4 d	 (88)	1166
		NBS, CH_2Cl_2, MS, rt, 1 h	 (89) α:β = 13:87	407
C_{31} 		$HgBr_2$	 (87) R = 	1142
		$HgCl_2$	 (92)	1142
		$HgBr_2$, C_6H_6, rt, 3 h	 (39) + N^7-β-isomer (28)	1142
C_{32} 		$(TfO)_2O$, $Cl(CH_2)_2Cl$	 (30)	412
		NBS, CH_2Cl_2, MS, rt		407
R^1				
α-SC_6H_4Cl-*p*		6 h	(90) α:β = 25:75	
SPh		7 h	(92) α:β = 92:8	
β-SPh		0.5 h	(87) α:β = 8:92	
α-SPh		5 h	(92) α:β = 26:74	
		NBS, CH_2Cl_2, MS, rt, 6 h	 (88) α:β = 84:16	407
		NBS, CH_2Cl_2, MS, rt, 2.5 h	 (81) α:β = 10:90	407
		NBS, CH_2Cl_2, MS, rt, 2.5 h	 (85) α:β = 11:89	407

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

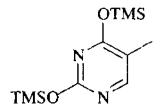
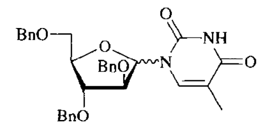
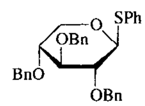
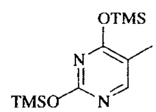
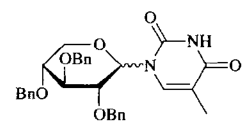
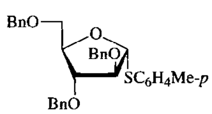
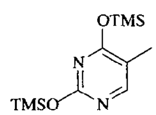
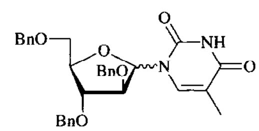
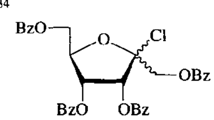
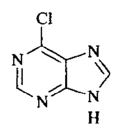
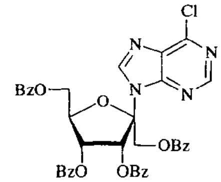
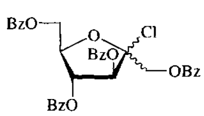
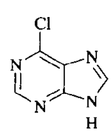
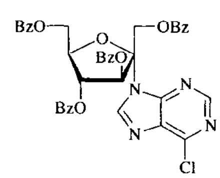
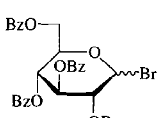
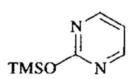
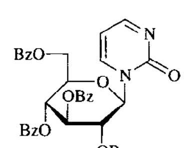
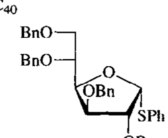
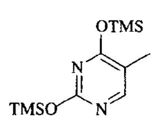
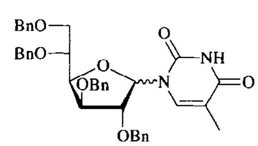
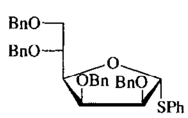
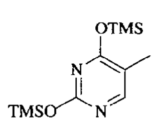
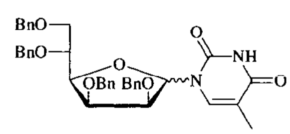
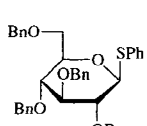
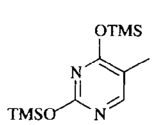
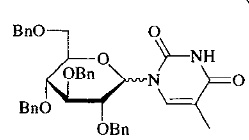
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		NBS, MS, rt		407
		CH_2Cl_2, 4.5 h	(89) α:β = 13:87	
		Et_2O, 2.5 h	(85) α:β = 21:79	
		THF, 2.5 h	(91) α:β = 47:53	
		MeCN, 5 h	(92) α:β = 26:74	
		C_6H_6, 5 h	(93) α:β = 16:84	
		$CHCl_3$, 3.5 h	(91) α:β = 9:91	
		NBS, CH_2Cl_2, MS, rt, 6.5 h	 (88) α:β = 93:7	407
C_{33}				
		NBS, CH_2Cl_2, MS, rt, 2.5 h	 (95) α:β = 26:74	407
C_{34}				
		$Hg(CN)_2$, $MeNO_2$, MS, 110°, 5 h	 (61)	920, 918
		$Hg(CN)_2$, $MeNO_2$, MS, 110°, 5 h	 (82)	920, 918
		MeCN, reflux, 8 h	 (48)	1187
C_{40}				
		CH_2Cl_2, rt		407
		NBS, MS, 26 h	(87) α:β = 96:4	
		NIS, TMSOTf, 0.5 h	(78) α:β = 57:43	
		DMTST, 5 h	(74) α:β = 58:42	
		NBS, CH_2Cl_2, MS, rt, 0.5 h	 (86) α:β = 14:86	407
		NBS, CH_2Cl_2, MS, rt, 45 h	 (78) α:β = 79:21	407

TABLE VIII. REACTIONS OF SILYLATED BASES WITH PROTECTED SUGARS WITH OR WITHOUT CATALYSTS (*Continued*)

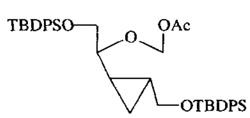
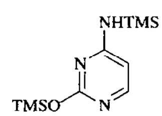
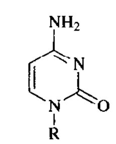
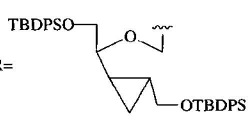
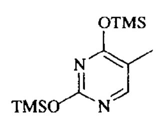
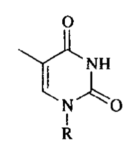
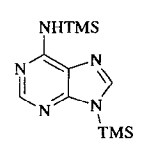
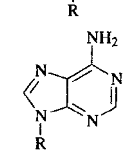
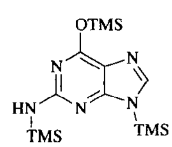
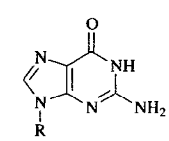
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{41} 		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 1 h	 (95) R= 	398
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 1 h	 (64)	398
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 2 h	 (55)	398
		KI, dibenzo-18-crown-6, MeCN, PhMe, 80°, 2 h	 (90)	398

TABLE IX. FUSION REACTIONS

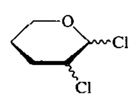
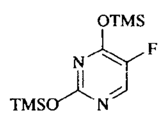
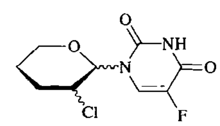
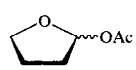
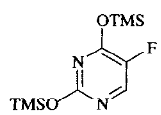
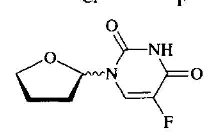
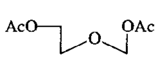
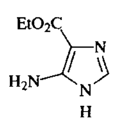
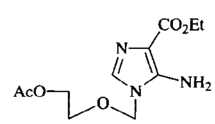
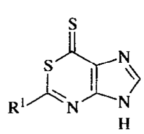
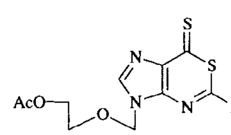
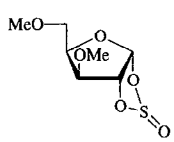
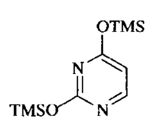
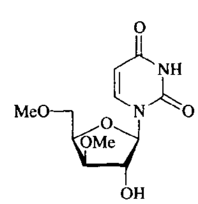
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		100-110°, 2 h	 (76)	552
C_6 		95-105°, 12 h	 (63)	528
C_7 		140°, 2 h	 (19) + N^3-isomer (27)	1191
		150°, 20 min 160°, 20 min 150°, 20 min	 R^1: Me (94); NHBn (56); Ph (55) + N^7-isomer (38)	1126
		90-120°, 18 h	 (80-89)	1192

TABLE IX. FUSION REACTIONS (*Continued*)

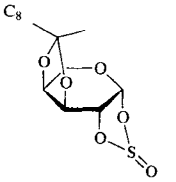
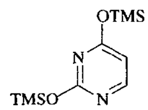
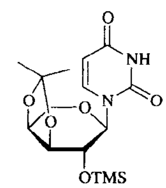
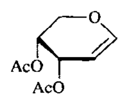
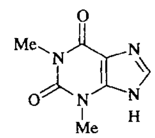
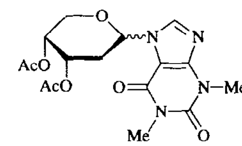
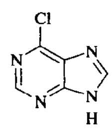
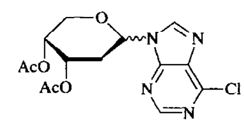
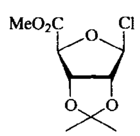
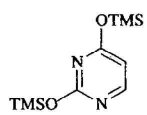
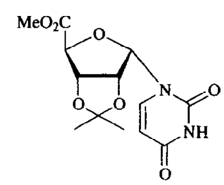
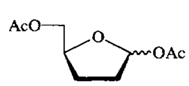
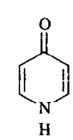
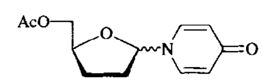
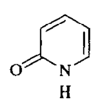
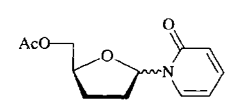
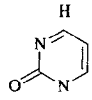
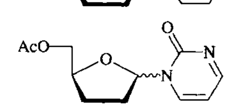
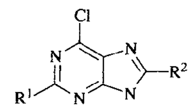
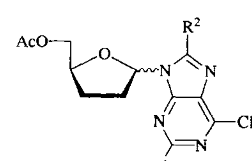
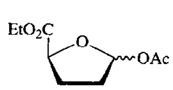
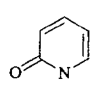
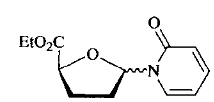
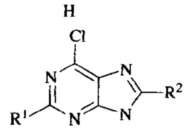
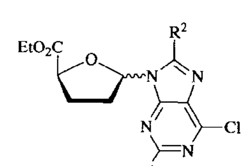
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		120°, 18 h	 (83)	1192
C_9 		TsOH, 120°	 (—)	307
		TsOH, 120°	 (—)	307
		140°, 3 d	 (58)	224
		115°, 1 h	 (34) α:β = 1:1	55
		110°, 1 h	 (38) α:β = 1:1	55
		115°, 20 min	 (35) α:β = 1:1	55
		115°		55
	R^1 R^2			
	H H	25 min	(84) α:β = 1:1	
	Cl H	15 min	(70) α:β = 1:1	
	Cl Cl	15 min	(82) α:β = 2:1	
		120°, 70 min	 (30) α:β = 1:1	55
				55
	R^1 R^2			
	H H	110-115°, 25 min	(59) α:β = 1:1	
	Cl H	110°, 20 min	(42) α:β = 1:1	
	Cl Cl	110°, 20 min	(51) α:β = 1:1	

TABLE IX. FUSION REACTIONS (*Continued*)

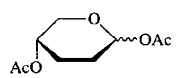
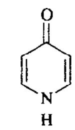
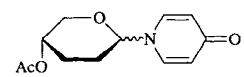
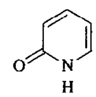
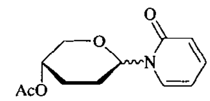
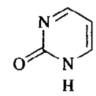
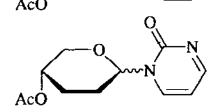
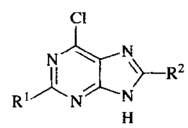
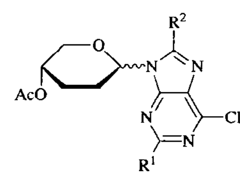
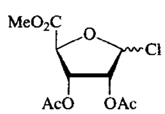
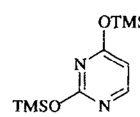
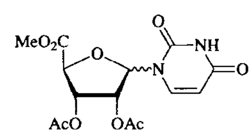
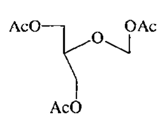
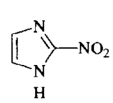
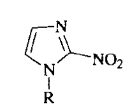
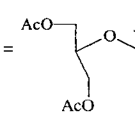
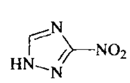
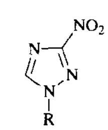
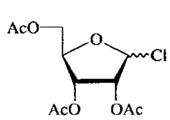
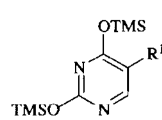
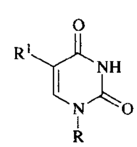
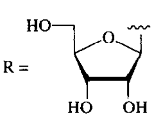
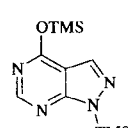
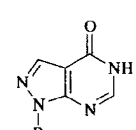
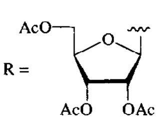
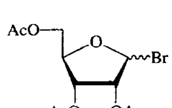
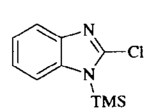
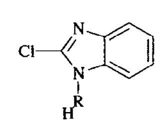
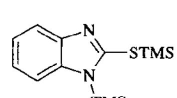
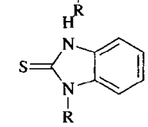
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		125°, 90 min	 (20) α:β = 1:1	55
		120°, 45 min	 (24) α:β = 1:1	55
		120°, 90 min	 (42) α:β = 1:1	55
				55
	R^1 R^2			
	H H	118°, 30 min	(83) α:β = 1:1	
	Cl H	120°, 20 min	(64) α:β = 1:1	
	Cl Cl	120°, 20 min	(72)	
		110°, 18 h	 (34) α:β = 1:3	224
		TsOH, 130-140°, 15 min	 (89) R = 	1193
		TsOH, 130-140°, 15 min	 (83)	1193
C_{11} 		1. 180-190° 2. NaOMe, MeOH	 R^1: H (35), Me (46); R = 	75
		180-190°	 (12) R = 	75
		110°, 30 min	 (69)	1194
		110°, 45 min	 (34)	1194

TABLE IX. FUSION REACTIONS (*Continued*)

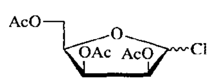
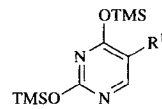
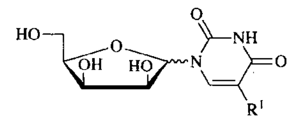
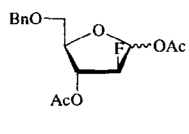
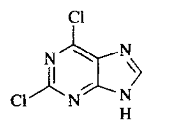
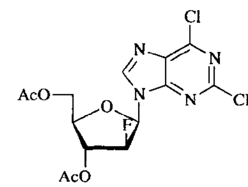
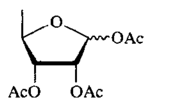
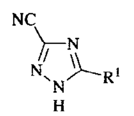
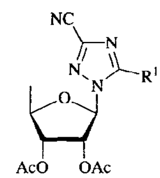
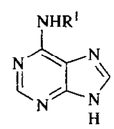
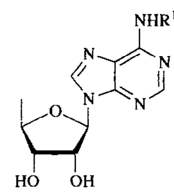
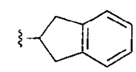
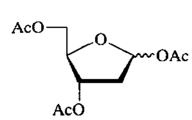
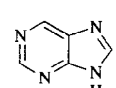
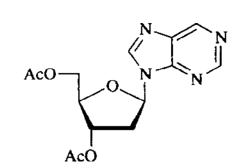
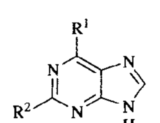
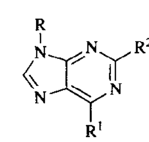
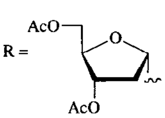
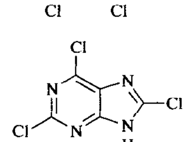
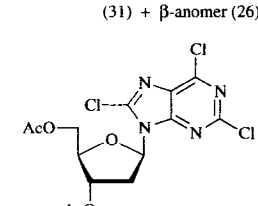
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. 190°, 40 min 2. NaOMe, MeOH		1195
	R^1			
	H		(—) α:β = 78:22	
	Me		(—) α:β = 2:1	
		TsOH, 160°, 20 min	 (30) + α-anomer (29)	1196
		$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 120°		1197
			R^1	
			H (84)	
			Cl (34) + N^2-isomer (25)	
		1. H_2SO_4, 180-195°, 4 h 2. NaOMe, MeOH, rt, 4 h		1198
	R^1			
	(*S*)-$PhCH(Me)CH_2$		(19)	
	C_6H_{11}		(18)	
	Ph_2CHCH_2		(8)	
			(19)	
		1. $ClCH_2CO_2H$, 140-145°, 18 min 2. NH_3, MeOH	 (18) + α-anomer (15)	1199
			 R = 	
	R^1 R^2			
	Cl H	$ClCH_2CO_2H$, 125-127°, 4 min	(21) + β-anomer (6)	1199
	Me H	Cl_2CHCO_2H, 150°, 15-20 min	(25)	1199
	NHBz H	Cl_2CHCO_2H, 160-165°, 25 min	(20) $R^1 = NH_2$	1199
	Cl Cl	130-140°, 15 min	(31) + β-anomer (26)	343
		$ClCH_2CO_2H$, 105°, 5 min	 (30)	1199

TABLE IX. FUSION REACTIONS (*Continued*)

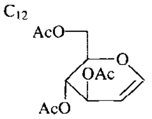
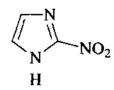
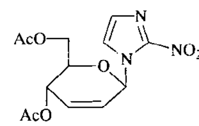
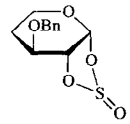
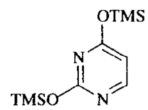
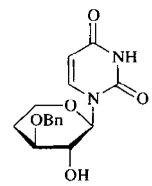
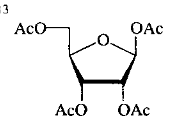
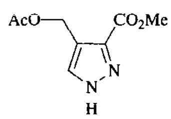
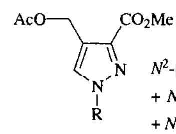
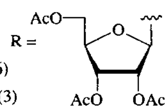
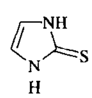
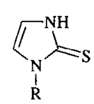
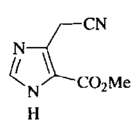
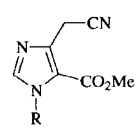
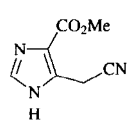
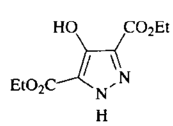
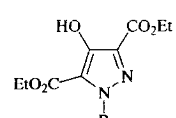
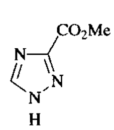
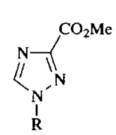
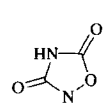
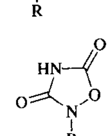
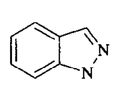
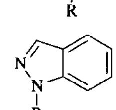
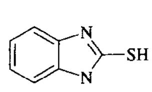
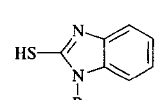
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 		$ZnCl_2$, 140-160°, 45 min, water aspirator	 (14) + α-anomer (10)	760
		90°, 4 h	 (94)	1192
C_{13} 		Br_2CHCO_2H, 155-160°, 50 min	 (41) + N^2-β-isomer (16) + N^1-α-isomer (3) + N^2-α-isomer (2) R = 	1200
		I_2 (0.07 eq), sugar:base = 2:1, 183°, 20 min	 I (68) + bis(riboside) (5)	701
		I_2 (0.052 eq), sugar:base = 1:1, 183°, 20 min	I (75) + bis(riboside) (11)	701
		1. 170°, 7-8 min 2. $ClCH_2CO_2H$, 190°, 5 min	 I (37) + N^3-isomer (<10)	707
		1. 170°, 7-8 min 2. $ClCH_2CO_2H$, 190°, 25 min	I (—) + N^3-β-isomer (10)	705, 707
		$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 170-175°, 25 min	I (47) + α-anomer (5) + N^3-β-isomer (19) + N^3-α-isomer (12)	705, 704
		I_2, 165°	 (80)	1201
		$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 160-165°, 15-20 min	 (78) + N^4-isomer (7)	259
		$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 120-125°, 1 h	 (75)	699
		I_2, 160°, 10 min	 I (48) + α-anomer (12) + N^2-β-isomer (23) + N^2-α-isomer (2)	1202
		$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 160°, 10 min	I (45) + α-anomer (10) + N^2-β-isomer (27) + N^2-α-isomer (4)	1202
		I_2, 200°, 12 mm vac., 12 min	 (44)	727

TABLE IX. FUSION REACTIONS (*Continued*)

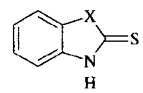
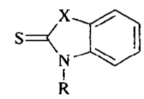
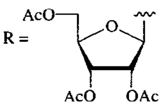
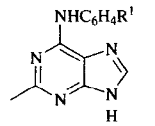
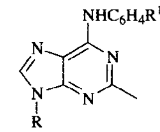
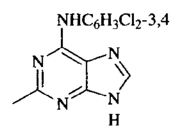
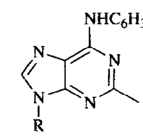
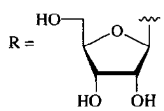
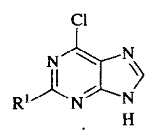
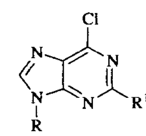
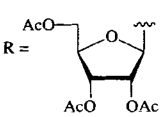
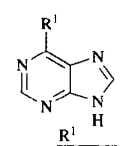
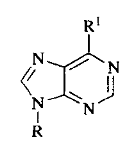
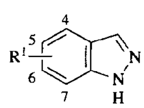
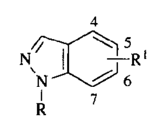
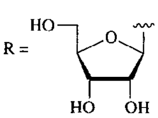
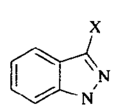
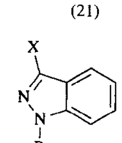
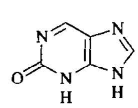
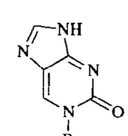
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		I_2, 160°, 12 mm vac., 20 min	 X: O (47); S (75); R = 	727
		1. 250°, 5 min 2. TsOH, 190° (10 mm Hg), 45 min 3. NH_3, MeOH		1203
	R^1			
	H		(49)	
	p-F		(49)	
	p-Cl		(55)	
	m-CF_3		(28)	
	p-Me		(41)	
	p-Et		(47)	
		1. 250°, 5 min 2. TsOH, 190° (10 mm Hg), 45 min 3. NH_3, MeOH	 (33) R = 	1203
			 R = 	
	R^1			
	Cl	I_2, 130-135°, 15 min	(90)	1204
	SO_2F	$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 145°, 1 h	(71)	950
				
	R^1			
	SO_2F	120°, 5 min	(22)	951
	SO_2NH_2	$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 150°, 1 h	(22)	951
		1. TsOH, 160°, 20 min 2. NaOMe, MeOH, rt, 12 h	 R = 	1205
	R^1			
	4-Cl		(32)	
	5-Cl		(45)	
	5-Br		(47)	
	6-Cl		(47)	
	5,6-Cl_2		(21)	
		1. TsOH, 20 min 2. NaOMe, MeOH, rt, 12 h		1205
	X			
	Cl	1. 160°	(50)	
	Cl	1. 150°	(31)	
	Br	1. 160°	(35)	
	I	1. 160°	(47)	
		1. H^+, 160°, 15 min 2. NH_3, MeOH	 (9)	1206

TABLE IX. FUSION REACTIONS (*Continued*)

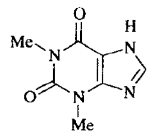
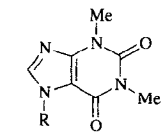
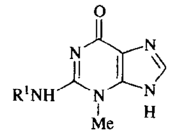
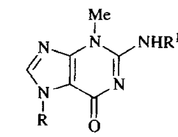
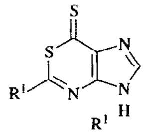
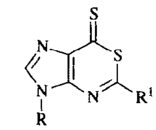
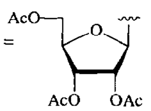
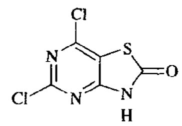
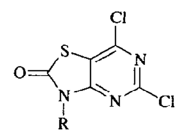
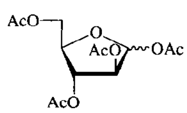
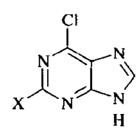
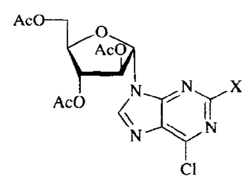
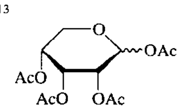
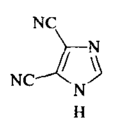
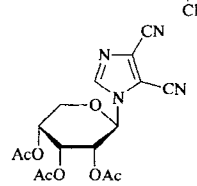
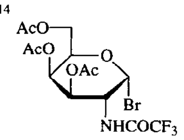
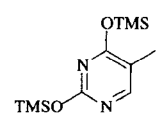
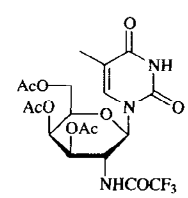
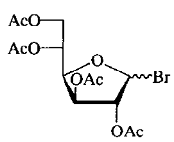
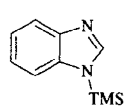
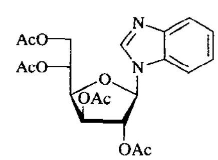
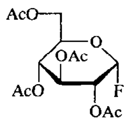
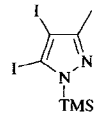
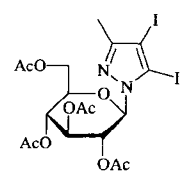
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. 130-150° 2. NH_3, MeOH	 (39)	1207
		TsOH	 R^1 — Ac: 220°, 15 min (39); *i*-Bu: 190°, 45 min (32)	1208
			 R = 	1209
	R^1			
	NH_2	150°, 3 h	(46) + N^7-isomer (10)	
	NHBn	160°, 3 h	(47) + N^7-α-anomer (14) + N^7-β-isomer (8)	
	Me	150°, 6 h	(49) + α-anomer (32) + N^7-α-isomer (9)	
	Ph	150°, 6 h	(44) + α-anomer (41) + N^7-isomer (5)	
		$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 170°, 10 min	 (80)	1058
		TsOH, 140°, 30 min	 X — F (85); Cl (75)	343
C_{13} 		$ClCH_2CO_2H$, 190-195°	 (26) + α-anomer (2)	161
C_{14} 		120-130°, 20 min	 (80)	1210
		Neat	 (36) + α-anomer (10)	1211
		180°, 20 min, vac.	 (10)	754

TABLE IX. FUSION REACTIONS (*Continued*)

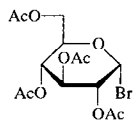
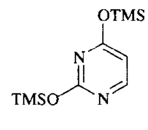
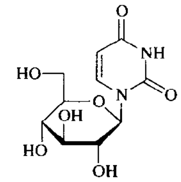
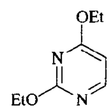
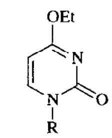
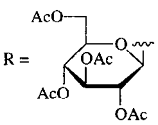
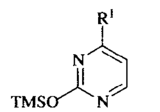
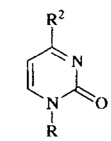
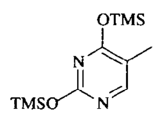
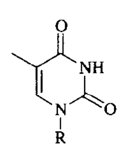
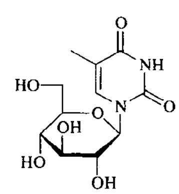
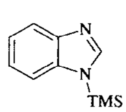
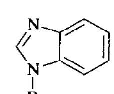
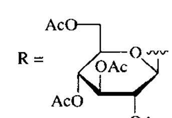
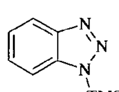
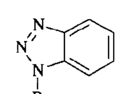
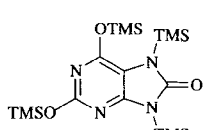
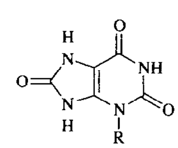
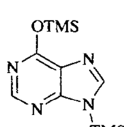
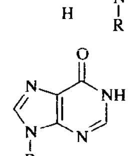
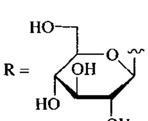
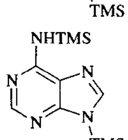
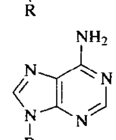
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. 180-190° 2. NaOMe	 (28)	75
		65°, 4 d, reduced pressure	 I (50) + α-anomer (19) R = 	1212
		65°, 12 h	I (—)	71
				
	R^1		R^2	
	NHTMS	180-190°	NH_2 (15)	75
	AcNTMS	185-190°	NHAc (15)	76
		185-190°	 I (52)	76
		100°, 3 h	I (41)	80
		1. 180-190° 2. NaOMe	 (43)	75
		110-130°	 (22) R = 	1213
		110-130°, 1 h	 (39)	1214
		NaI	 (—)	73
		1. 180-190° 2. NaOMe	 (16) R = 	75
		1. 180-190° 2. NaOMe	 (5)	75

TABLE IX. FUSION REACTIONS (*Continued*)

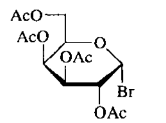
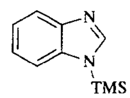
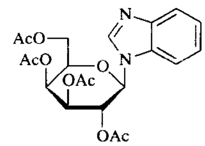
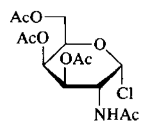
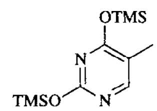
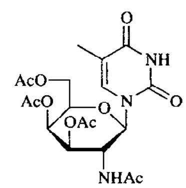
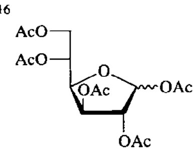
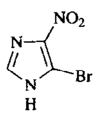
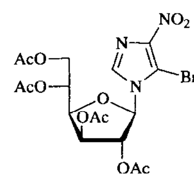
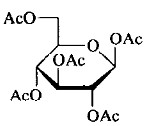
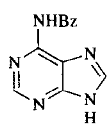
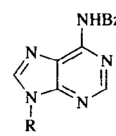
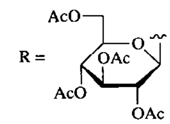
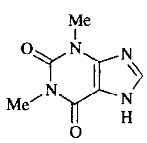
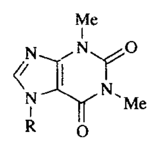
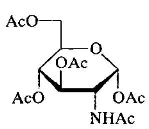
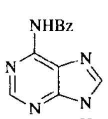
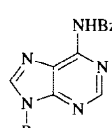
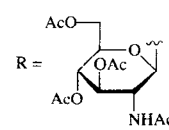
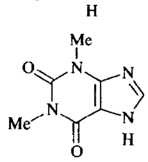
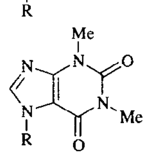
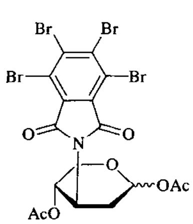
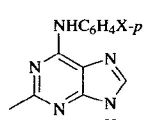
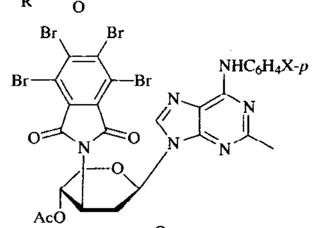
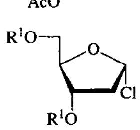
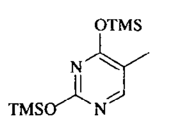
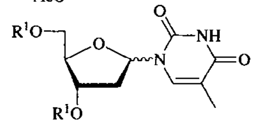
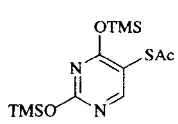
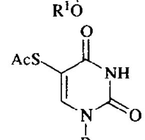
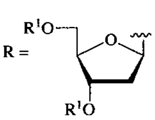
Sugar	Base	Conditions	Product(s) and Yield(s) (%)		Refs.
		110-130°		(33) + α-anomer (20)	1215
		130-140°		(40)	1210
C_{16} 		H_2NSO_3H, 200-210°, 10 min		(30)	1210a
		TsOH, 160°, 4 h	 (32)	R = 	1071
					1207
		p-$O_2NC_6H_4OH$, TsOH, 130-135°, 5 h	(90)		
		$TsNH_2$, 160°, 3 h	(71)		
		o-$O_2NC_6H_4CO_2H$, 150-155°, 3 h	(70)		
		TsOH, 155-160°, 4 h	 (8-14)	R = 	1071
		p-$O_2NC_6H_4OH$, TsOH, 130°, 4 h	 (45)		1071
C_{17} 		TsOH, 190°, 45 min		X: Cl (49); H (37)	1216
C_{19}  $R^1 = p$-ClC_6H_4CO		100-110°, 15-20 min		(34) α:β = 1:3.3	266
		100-110°, 15-20 min	 (87)	R = 	266

TABLE IX. FUSION REACTIONS (*Continued*)

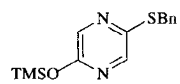
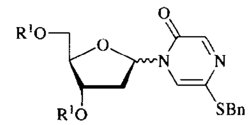
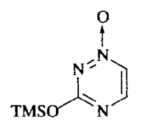
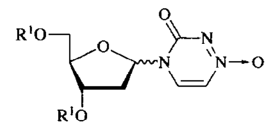
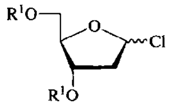
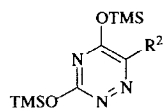
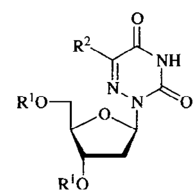
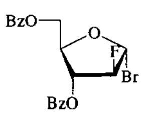
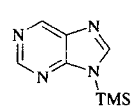
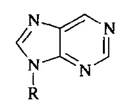
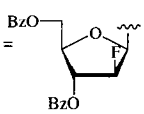
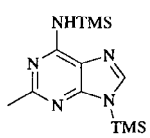
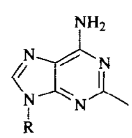
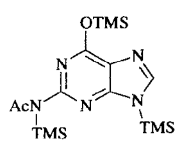
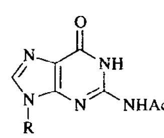
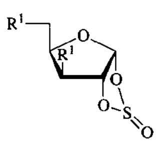
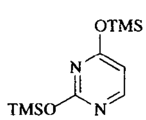
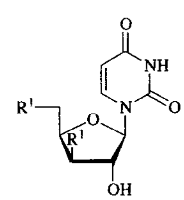
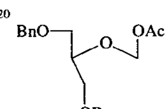
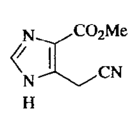
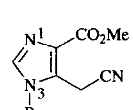
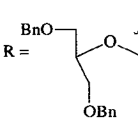
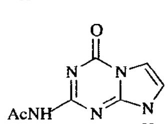
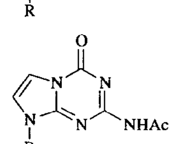
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		95-110°, 0.05 mm Hg, 20 min	 (70) α:β = 4:1	1217
		100-110°, 20 min 2.6-3.3 kPa	 (27)	1218
 $R^1 = p\text{-}O_2NC_6H_4CO$				
	R^2			
	Br	Heat	(86)	1219
	Br	130°, 0.5 h	(—)	1220
	CF_3	Heat	(51)	1219
	CF_3	150°, 15 min	(33)	1220
	Me	150°, 30 min, 25 mm Hg	(86)	1221
		100°, 45 min	 (48) + N^7-isomer (16) R = 	1222
		100°, 45 min	 (55) + N^7-isomer (16)	1222
			 (—) + α-anomer (—) + N^7-α & β-isomers (—)	1223
				1192
R^1				
BzO		125°, 18 h	(92)	
BzO		90°, 20 h	(68) + α-anomer (20)	
BnO		115°, 18 h	(92)	
BnO		90°, 18 h	(70) + α-anomer (10)	
C_{20} 		$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 110°, 4 h	 (19) + N^1-isomer (31) R = 	1224
		H^+, 95°, 12 h; 120°, 16 h	 (40)	838

TABLE IX. FUSION REACTIONS (*Continued*)

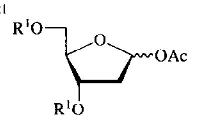
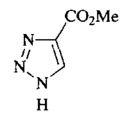
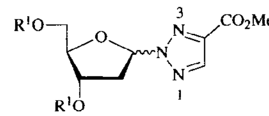
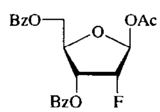
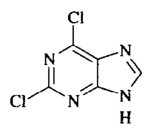
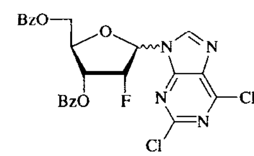
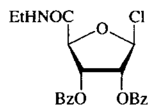
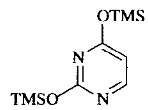
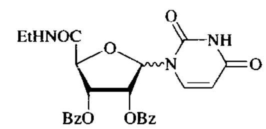
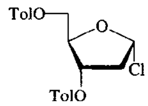
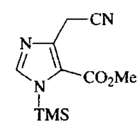
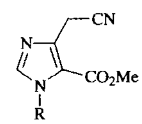
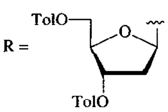
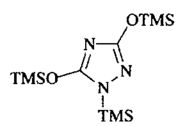
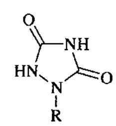
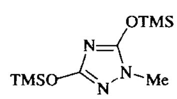
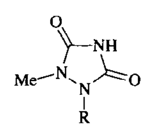
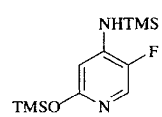
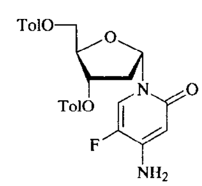
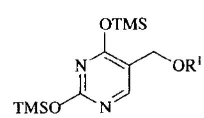
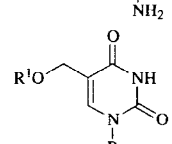
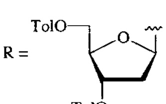
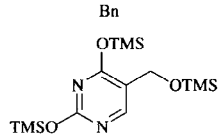
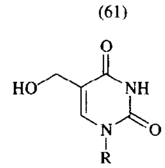
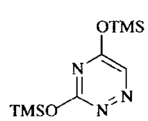
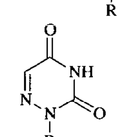
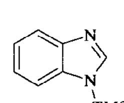
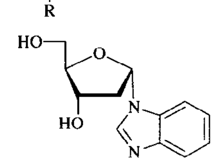
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}  $R^1 = p\text{-}O_2NC_6H_4CO$		$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 143°, 20 min, reduced pressure	 (52) + N^1-β-isomer (12)	842
		TsOH, 160°, 50 min	 (45) α:β = 1:1	1225
		110°, 3 h	 (71) α:β = 3:7	224
		179-180°	 (25) R = 	802a
		110°, 30 min	 (67)	258
		110°, 15 min	 (41)	258
		120°, 10 mm, 25 min	 (15) + β-anomer (13)	1226
		185-195°, 30 min	 R = 	1227
	R^1			
	Me		(70) + α-anomer (—)	
	Et		(73) + α-anomer (—)	
	Pr-*n*		(86)	
	Bu-*n*		(88)	
	Bn		(61)	
		185-195°, 30 min	 (58)	1177
		95-100°, 30 min	 (25)	1179
		1. 115°, 17 min 2. NaOMe, MeOH	 (24) + β-anomer (9)	816

TABLE IX. FUSION REACTIONS (*Continued*)

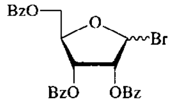
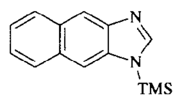
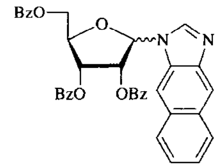
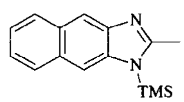
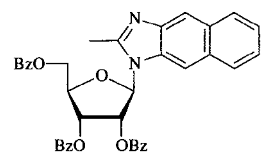
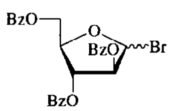
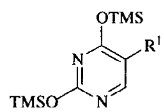
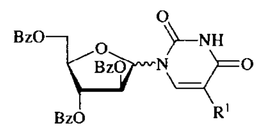
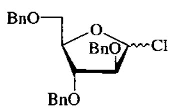
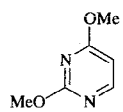
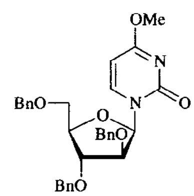
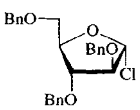
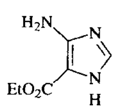
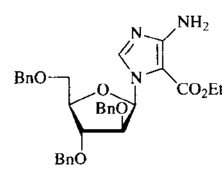
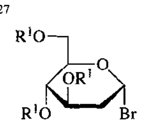
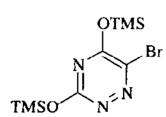
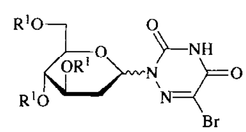
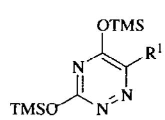
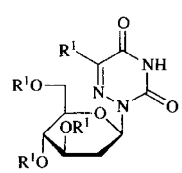
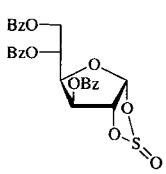
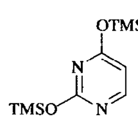
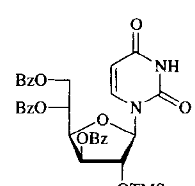
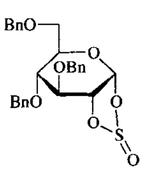
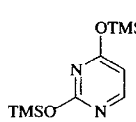
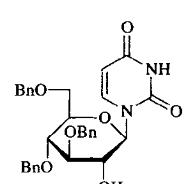
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26} 		KI, 130°, 1 h	 (90)	1228
		KI, 130°, 1 h	 (41) + α-anomer (16)	1228
		190°, 40 min	 R^1: H (—) α:β ~ 3:1; Me (—) α:β = 7:2	1195
		100°, 20 h	 (—)	356
		110°, 1 min	 (2)	352
C_{27}  R^1 = p-$O_2NC_6H_4CO$		105°, 2 d	 (43)	1229
			 R^1: H 100°, 25 h (32); Me 90°, 12 h (44)	1230; 1230
		120°, 6 h	 (93)	1192
		125°, 18 h	 I (91)	1192

TABLE IX. FUSION REACTIONS (*Continued*)

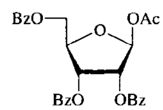
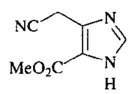
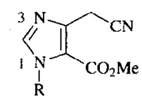
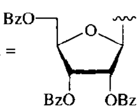
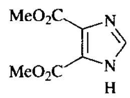
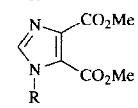
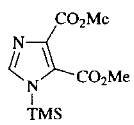
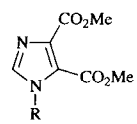
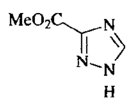
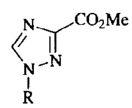
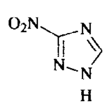
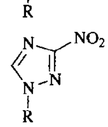
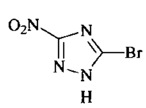
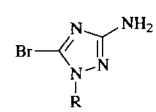
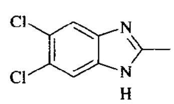
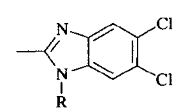
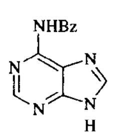
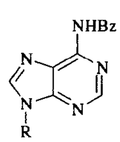
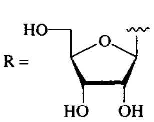
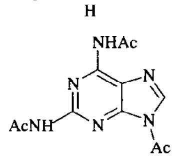
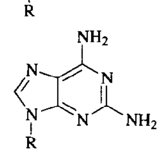
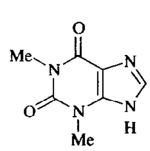
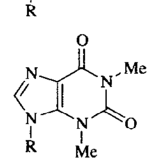
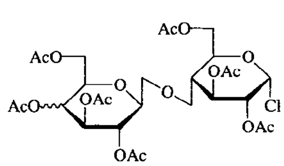
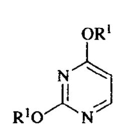
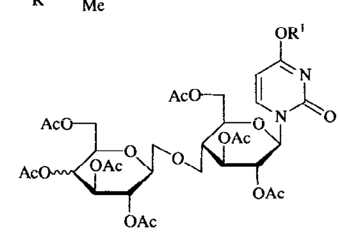
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. 179°, 7-8 min 2. $ClCH_2CO_2H$, 190°, 25 min	 $N^1 + N^3$ isomers (47) R = 	705
		$(p\text{-}O_2NC_6H_4O)_2P(O)OH$	 (42) + α-anomer (6)	852
		200°, 30 min	 (—)	853
		$(p\text{-}O_2NC_6H_4O)_2P(O)OH$, 160-165°, 15-20 min	 (~78) + N^2-isomer (~8)	259
		190°, 30 min	 (88)	258
		1. 150°, 30 min 2. H_2, Pd/C	 (60)	258
		TsOH, 160-165°, 40 min	 (25)	849
		1. I_2, 140-145°, 20 min 2. NaOMe, $CHCl_3$, reflux, 30 min	 (45) R = 	1204
		1. I_2, 170-175° 2. NaOMe, $CHCl_3$, NH_3	 (59)	1204
		1. I_2, 160-165° 2. NaOMe, $CHCl_3$	 (81)	1204
				
	R^1			
	Me	125-130°, 60 h	(42)	1231
	Et	120-125°, 6 d	(46)	1231

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS

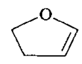
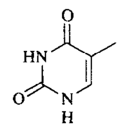
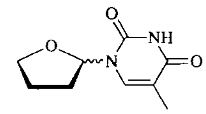
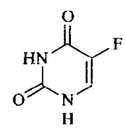
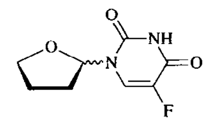
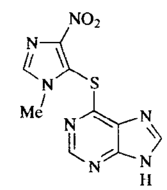
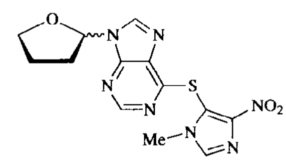
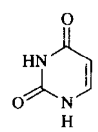
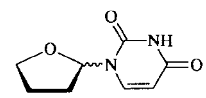
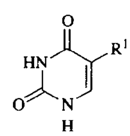
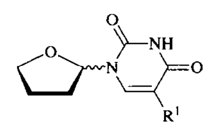
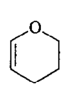
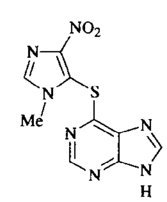
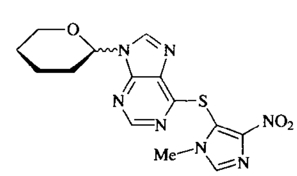
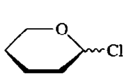
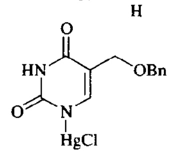
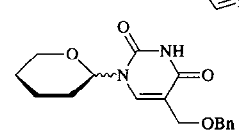
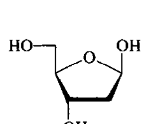
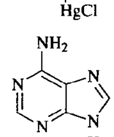
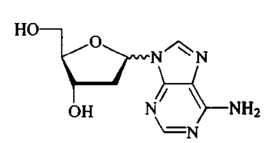
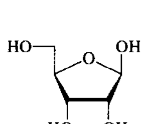
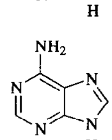
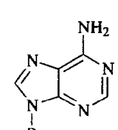
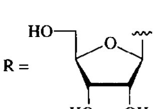
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		Me_2SiCl_2, Et_3N, MeCN, rt, 1 h	 (84)	1232
				
		Py•HCl, Py, 120°, 20 h	(90)[a]	1067
		Al_2O_3, Py, 130°, 24 h	(89)	1067
		Py, 150°, 8 h, autoclave	(88)	1067
		DMA, 180°, 5 h, autoclave	(86)	1067
		Me_2SiCl_2, Et_3N, MeCN, 30-35°, 2 h	(86)	1232
		TsOH, EtOAc, 50°, 24 h	 (86)	1092
		PCl_5, HMPA, rt, 5 h	 (92)	1233
		PCl_5, HMPA, rt		1233
	R^1			
	F	30 min	(88)	
	Br	1.5 h	(54)	
	I	1.5 h	(59)	
	Me	1 h	(58)	
C_5				
		TsOH, EtOAc, 50°, 24 h	 (71)	1092
		PhMe, −30° to rt, 2 d	 (77)	551
		Phenyl polyphosphate, DMF, 50°, 10 min	 (40)	1234
		Phenyl polyphosphate, DMF, 50°, 10 min	 (20) R = 	1234

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

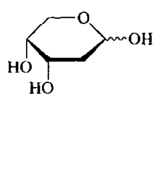
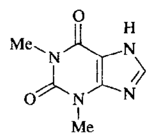
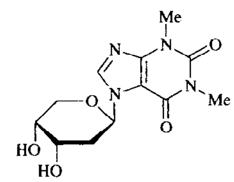
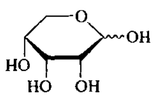
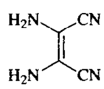
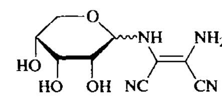
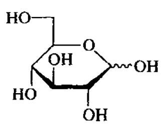
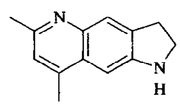
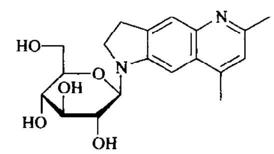
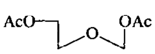
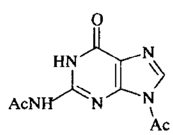
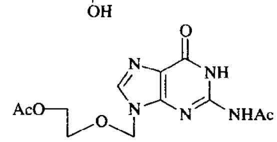
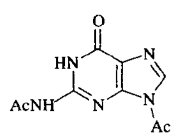
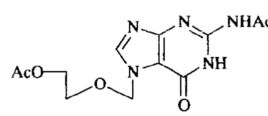
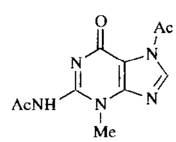
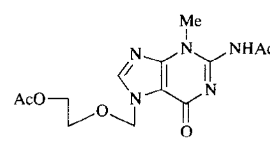
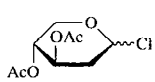
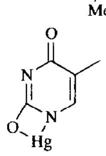
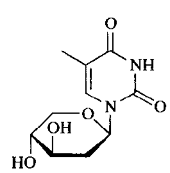
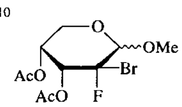
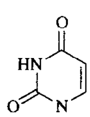
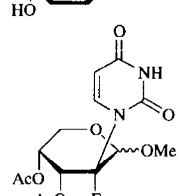
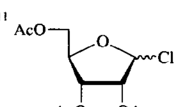
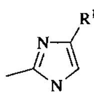
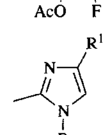
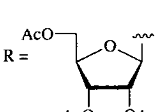
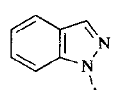
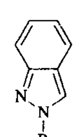
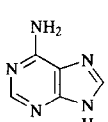
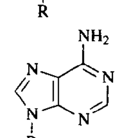
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		P_4O_{10}, Bu_3N, $CHCl_3$, 40°, 3 d	 (25) + α-anomer (20)	1235
		AcOH, MeOH, rt, 24 h	 (51)	161
C_6 		EtOH, reflux, 6 h	 (9)	1236
C_7 		DMSO, 100°		1237
		p-$H_2NC_6H_4SO_3H$[b]	(66) + N^7-isomer (28)	
		TsOH	(66) + N^7-isomer (26)	
		p-$O_2NC_6H_4SO_3H$	(59) + N^7-isomer (24)	
		TsOH, DMSO, 80°	 (53) + N^9-isomer (31)	1237
		TsOH, PhMe, reflux, 20 h	 (69)	1238
C_9 		1. DMF, PhMe, rt, 2 h 2. NH_3, MeOH	 (8) + α-anomer (7)	927
C_{10} 		HgO, $HgBr_2$, CH_2Cl_2	 (23)	1239
C_{11} 		$Hg(CN)_2$, $MeNO_2$, reflux, 3-4 h	 R^1: CO_2Et (35); $CONH_2$ (45); R = 	1240
		Xylene, reflux	 (42)	728
		DMF, rt, 4.5 d	 (18)	1241

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

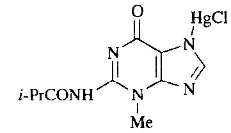
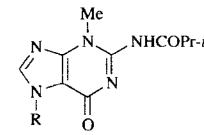
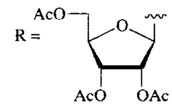
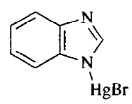
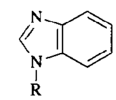
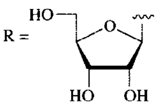
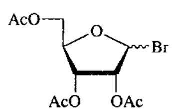
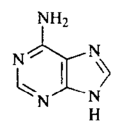
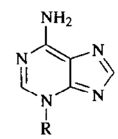
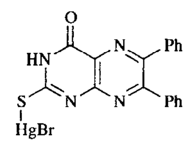
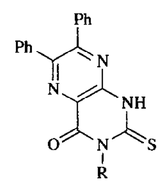
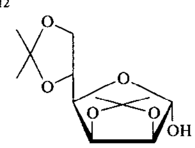
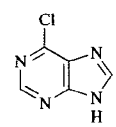
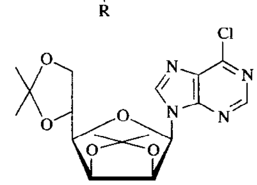
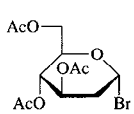
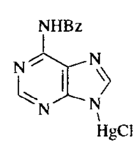
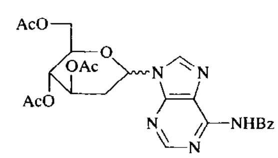
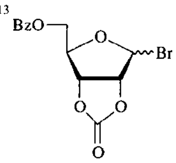
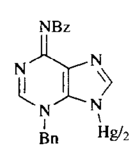
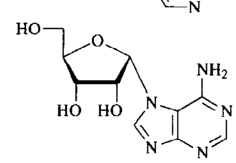
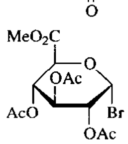
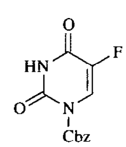
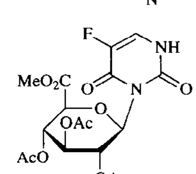
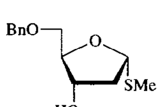
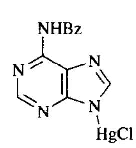
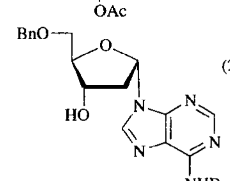
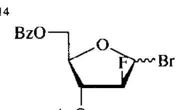
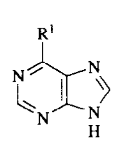
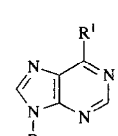
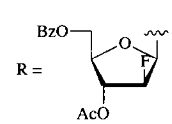
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		Xylene, reflux, 1 h	 (49) R = 	1208
		1. Xylene, reflux, 2 h 2. NH_3, MeOH, 18 h	 (53) R = 	1242
		MeCN, 50°, 36 h	 **I** (25) + N^9-isomer (18)	1243
		DMF, 90°, 1 h	**I** (20)	1241
		PhMe. reflux, 6 h	 (17)	1244
C_{12}				
		Ph_3PMe, DEAD, THF, rt, 12 h	 (63) + α-anomer (16)	430
		DMF, PhMe, rt, 8 h	 (—)	63
C_{13}				
		1. Xylene, reflux, 1 h 2. NaOMe, MeOH 3. H_2, Pd/C, 80°, 16 h	 (14) + β-anomer (8)	1245
		DMF	 (—)	770
		$Cl(CH_2)_2Cl$, reflux, 5 h	 (28) + β-anomer (20)	413
C_{14}				
		CH_2Cl_2, MS, reflux	 R = 	
	R^1			
	Cl	15 h	(8)	391
	NHBz	3 d	(34)	384, 1246

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

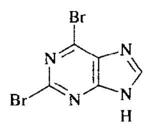
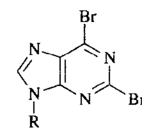
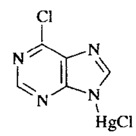
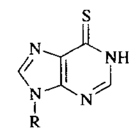
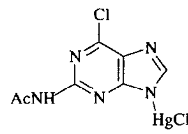
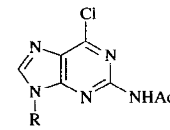
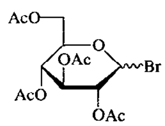
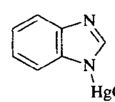
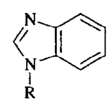
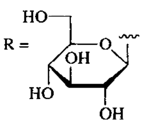
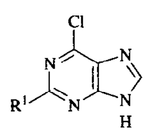
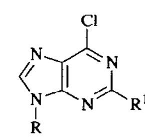
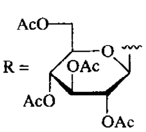
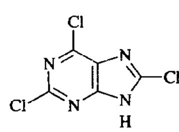
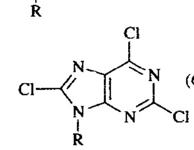
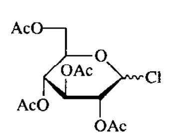
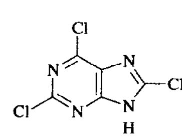
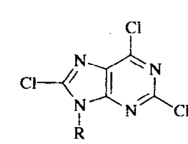
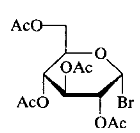
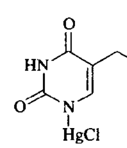
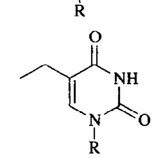
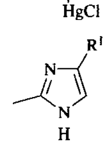
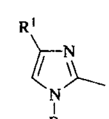
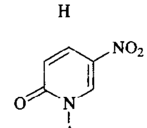
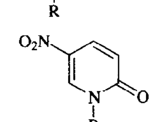
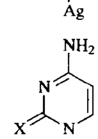
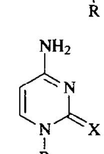
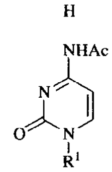
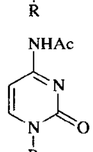
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cl(CH$_2$)$_2$Cl, MS, 100°, 32 h	 (32)	539
		1. Xylene, reflux, 12 h 2. thiouracil	 (10)	384
		Xylene, reflux, 15 h	 (17)	384, 1246
		1. Xylene, reflux, 1.5-2 h 2. NH$_3$, MeOH	 (34) R = 	1247
		Hg(CN)$_2$, MeNO$_2$, reflux, 2.5 h	 R^1: H (55); Cl (79) R = 	1247
		Hg(CN)$_2$, MeNO$_2$, reflux, 2 h	 (61)	1247
		Hg(CN)$_2$, MeNO$_2$, reflux, 3 h	 (68)	1247
		PhMe, reflux, 2 h	 (—)	1248
		Hg(CN)$_2$, MeNO$_2$, MS, reflux, 3-4 h	 R^1: CONH$_2$ (46); CO$_2$Et (36) + N^3-isomer (12)	1240
		PhMe, reflux, 20 min	 (~5)	58
		Hg(CN)$_2$, MeNO$_2$, MS, reflux, 1 h	 X: O (50); S (40)	1249
		Hg(CN)$_2$, HgBr$_2$, MeNO$_2$, PhMe, reflux, 20 min	 R^1 = H, (55)	1249

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

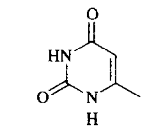
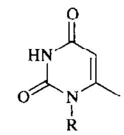
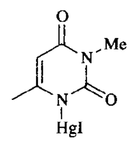
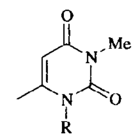
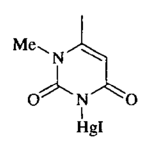
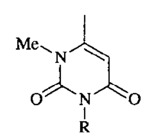
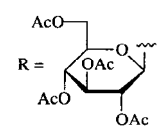
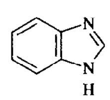
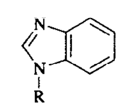
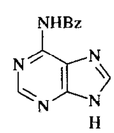
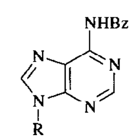
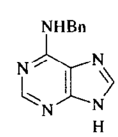
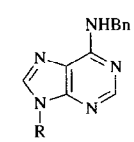
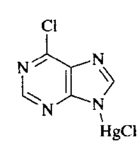
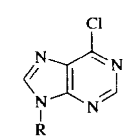
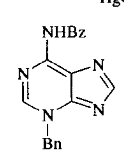
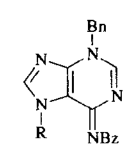
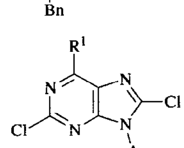
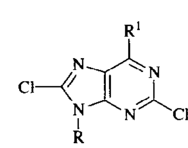
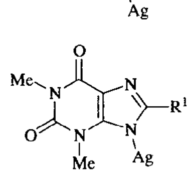
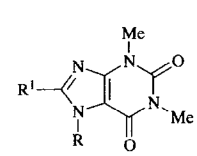
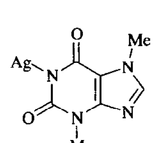
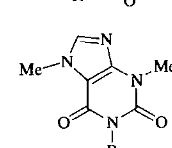
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$HgBr_2$, PhMe, reflux	R^1 = Ag, (55)	57
		$Hg(CN)_2$, $MeNO_2$, reflux, 4 h	 (94)	1249
		1. PhMe, reflux, 4 h 2. KI	 (7)	60
		PhMe, MeCN, reflux, 4 h	 (43) R = 	60
		$Hg(CN)_2$, $MeNO_2$, reflux, 4 h	 (63)	1247
		$Hg(CN)_2$, $MeNO_2$, reflux, 3 h	 (75)	1247
		DMF, 100°, 20 h	 (30) + N^3-isomer (—)	1250
		Xylene, reflux, 2 h	 (86)	1251
		Xylene, reflux, 1.5 h	 (28)	1251
		Xylene, reflux	 R^1: Cl — (—); NH_2 6 h (29)	56
		Xylene, reflux	 R^1: H 1 min (75); Cl 10 min (40)	56
		PhMe, reflux, 30 min	 (23)	56

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

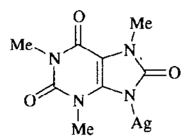
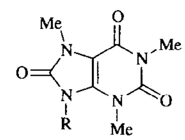
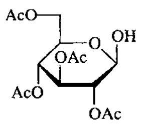
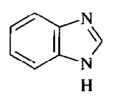
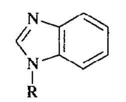
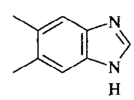
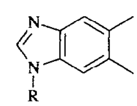
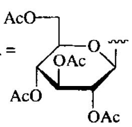
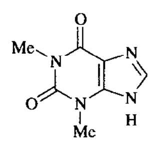
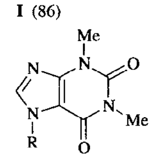
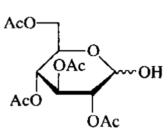
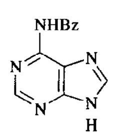
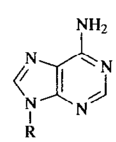
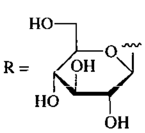
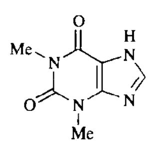
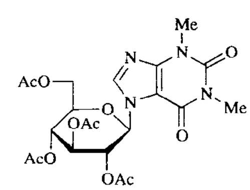
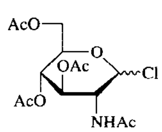
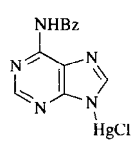
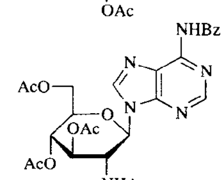
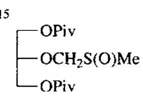
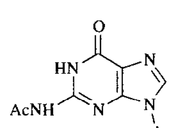
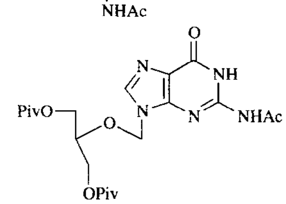
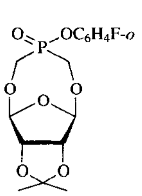
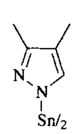
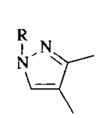
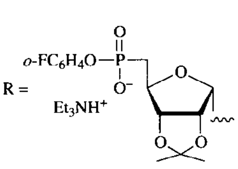
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		Xylene, reflux, 5 min	 (—)	56
		$Et_2O{\bullet}BF_3$, $Cl(CH_2)_2Cl$, 60°, 10 h	 I (73)	1252
		1. CETF, $Cl(CH_2)_2Cl$, $Et_3O^+BF_4^-$ 2. $Cl(CH_2)_2Cl$, DME, 60°, 10 h	I (73)	429
		1. $Cl(CH_2)_2Cl$, $Et_3O^+BF_4^-$ 2. $Cl(CH_2)_2Cl$, DME, 60°, 10 h	 I (86) R = 	429
		$Et_2O{\bullet}BF_3$	I (86)	1252
		1. CETF, $Cl(CH_2)_2Cl$, $Et_3O^+BF_4^-$ 2. $Cl(CH_2)_2Cl$, DME, 60°, 10 h	 (93)	429
		1. P_4O_{10}, DMF, 50-60°, 75 h 2. NH_3, MeOH	 (10) R = 	437
		P_4O_{10}, DMF, 60-70°, 20 h	 (48)	437
		$CdCO_3$, $CHCl_3$, reflux, 1.5 h	 (39)	1071
		TsOH, DMSO, DMF, 105°, 42 h	 (45) + N^7-isomer (17)	1253
		$Et_3NH^+HCO_3^-$, THF, rt, 2 d	 (57) R = 	433

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

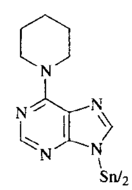
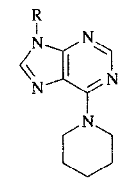
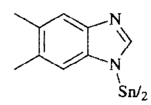
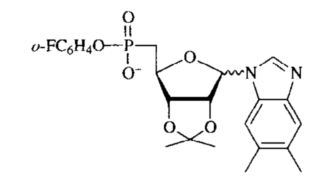
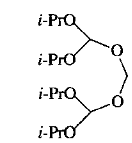
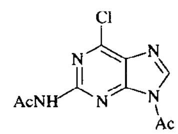
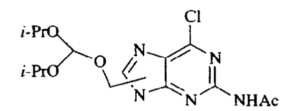
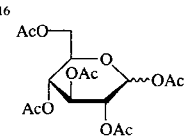
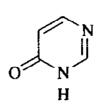
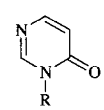
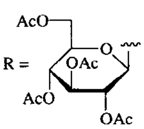
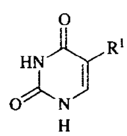
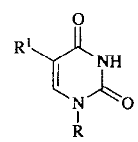
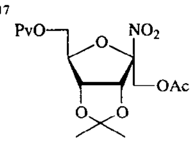
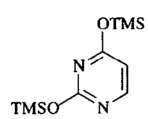
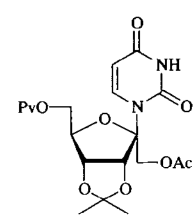
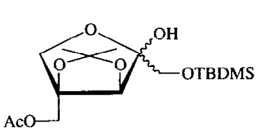
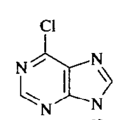
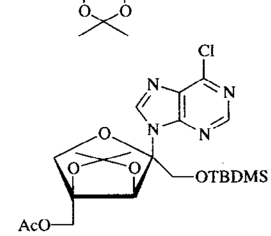
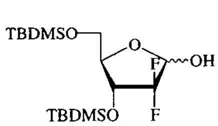
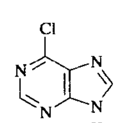
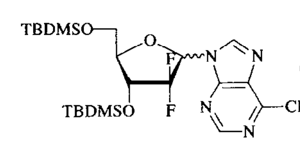
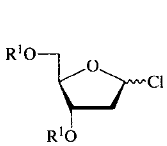
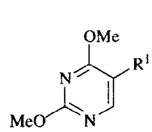
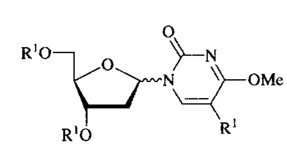
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Et_3NH^+HCO_3^-$, THF, rt, 4 d	 (30)	433
		$Et_3NH^+HCO_3^-$, THF, rt, 12 h	 (81) α:β = 95:5	433
		$Al_2(SO_4)_3$, *N*-methyl-pyrrolidin-2-one, 100°, 6 h	 (61) N^9:N^7 = 74:8	521
C_{16} 		$Hg(CN)_2$, $MeNO_2$, reflux, 6 h	 (52) R = 	516
		$Hg(CN)_2$, $MeNO_2$, reflux, 6 h	 R¹: Me (87); F (65); CO_2Et (85)	516
C_{17} 		$FeCl_3$, MeCN, 80°, 30 min	 (60) + α-anomer (17)	106
		Ph_2PMe, DEAD, THF, rt, 12 h	 (48)	430
		Ph_2PMe, DEAD	 (50) α:β = 1:1	431
C_{19}  R^1 = *p*-$O_2NC_6H_4CO$				2
	R¹: H	MeCN	(44) α:β = 5.7:1	
	H	C_6H_6	(35) α:β = 3.4:1	
	Me	MeCN	(39) α:β = 3.8:1	
	Me	C_6H_6	(36) α:β = 1.9:1	

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

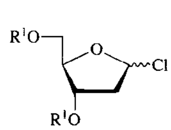
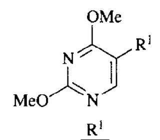
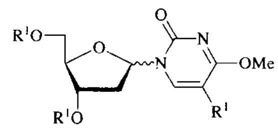
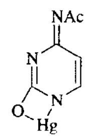
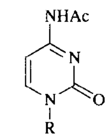
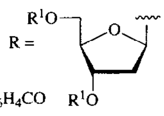
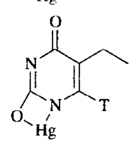
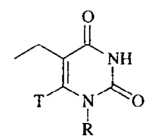
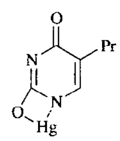
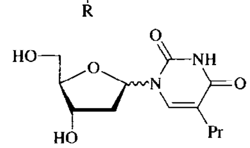
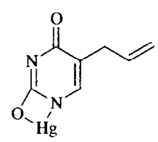
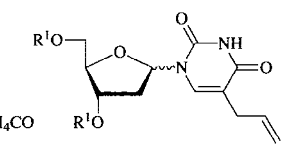
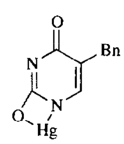
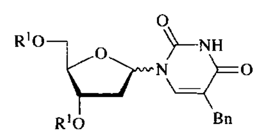
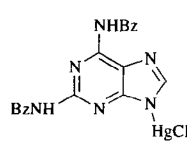
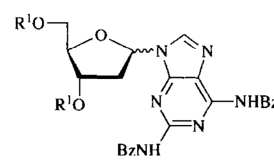
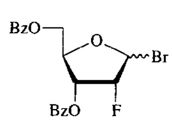
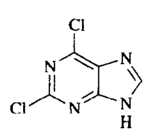
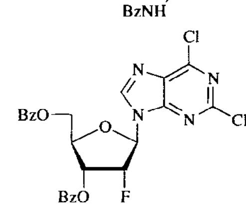
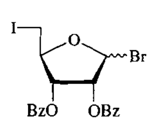
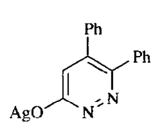
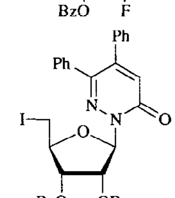
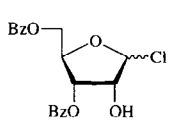
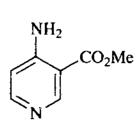
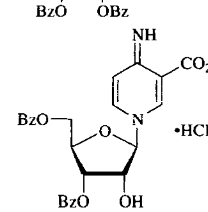
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
 $R^1 = p\text{-}ClC_6H_4CO$	 R^1			2
	H	MeCN	(50) $\alpha:\beta = 4.5:1$	
	H	C_6H_6	(31) $\alpha:\beta = 2.4:1$	
	Me	MeCN	(46) $\alpha:\beta = 3.6:1$	
	Me	C_6H_6	(39) $\alpha:\beta = 1.9:1$	
		1. Xylene, reflux 2. 0°	 (32) + α-anomer (22) R =  $R^1 = p\text{-}ClC_6H_4CO$	264
		1. PhMe, rt, 3 h 2. 60°, 1 h	 (80)	1254
		1. PhMe, reflux 2. NaOMe, MeOH, reflux, 2 h	 (89-90)	1255
		PhMe, reflux, 8 min	 (89-90) $R^1 = p\text{-}ClC_6H_4CO$	265
		PhMe, reflux, 1 h	 (80)	1256
		C_6H_6, reflux	 (38)	343
		$Hg(CN)_2$, $Cl(CH_2)_2Cl$, rt, 20 min	 (59) + α-anomer (2)	1225
		1. PhMe, reflux, 5 min 2. $HgBr_2$, PhMe, reflux, 5 h	 (36-42)	1257
		CH_2Cl_2, rt, 12 h	 (83)	1258

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

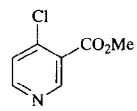
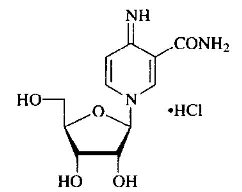
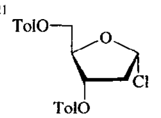
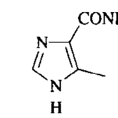
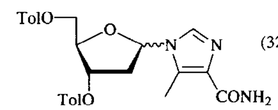
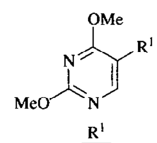
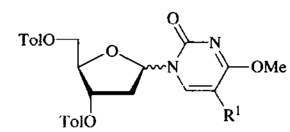
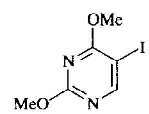
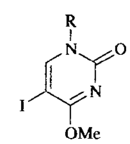
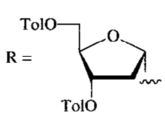
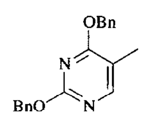
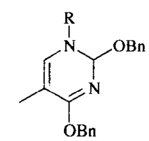
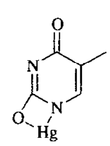
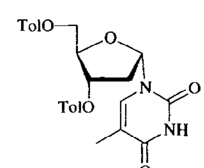
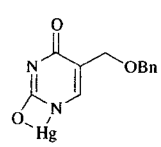
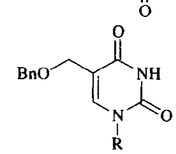
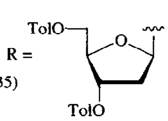
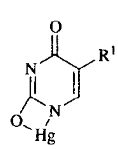
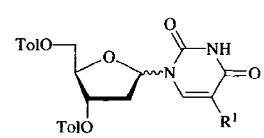
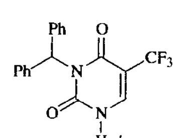
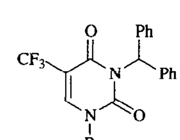
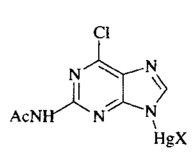
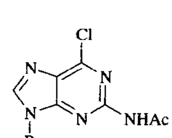
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CH_2Cl_2, 4°, 12 h 2. NH_3, MeOH, rt, 12 h	 (26)	1258
C_{21} 		$Hg(CN)_2$, $MeNO_2$, MS, reflux, 6 h	 (32) + N^3-isomer (6)	708
	 R^1 H Me	MeCN	 (53) α:β = 7.7:1 (72) α:β = 5.7:1	72
		$MeNO_2$, rt, 70 h	 I (18) + β-anomer (3) R = 	263
		MeCN, rt, 5 d	I (20) + β-anomer (4)	263
		CH_2Cl_2, rt, 24 h	 (55)	261
		DMF, PhMe, rt, 1 h	 (68) + β-anomer (23)	51
		PhMe, rt, 16 h	 (49) + α-anomer (35) R = 	1259
	 R^1			
	I	PhMe, DMF, rt, 18 h	(—)	263
	CN	MeCN, MS, 95°, 1 h	(—)	1260
	NO_2	PhMe, DMF, rt, 4 d	(—)	88
		PhMe, rt, 12 h	 (24)	1262
		C_6H_6, reflux, 1 h	 (25) + α-anomer (16)	1263

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

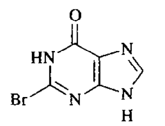
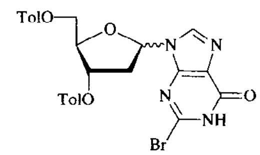
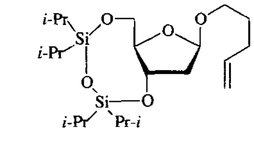
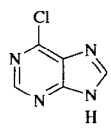
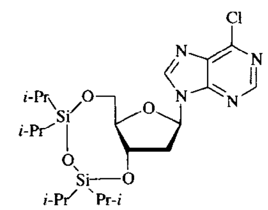
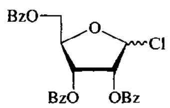
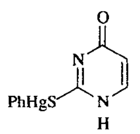
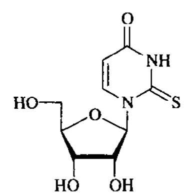
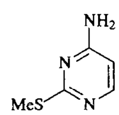
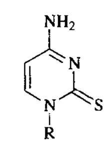
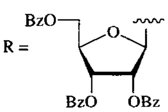
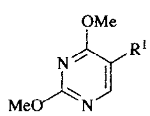
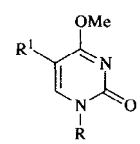
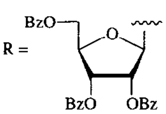
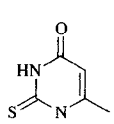
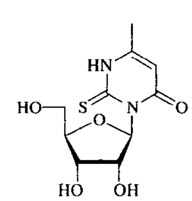
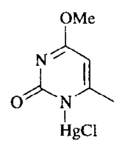
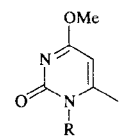
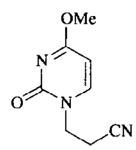
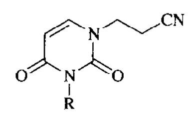
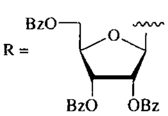
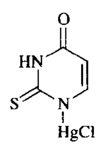
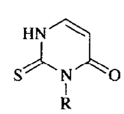
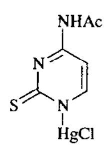
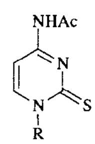
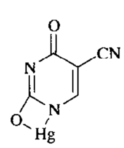
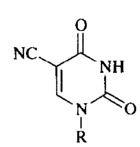
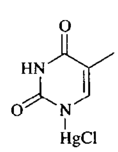
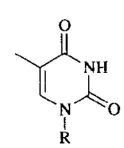
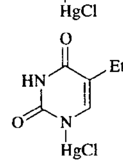
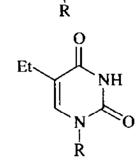
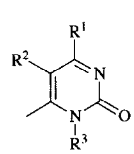
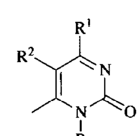
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
				1264
		DMF, rt, 24 h	(75) α:β = 1:37.5	
		CH_2Cl_2, rt, 24 h	(51) α:β = 1:2.6	
		DMSO, rt, 24 h	(70) α:β = 1:14	
C_{22} 		IDCP, MeCN, MS, rt, 2 h	 (20) + α-anomer (20)	421
C_{26} 		1. $Hg(CN)_2$, $MeNO_2$, reflux, 4 h 2. NaOMe, MeOH	 (45)	1265
		1. MeCN, MS, 30° 2. H_2S, Py	 (40) R = 	1266
			 R = 	
	R^1			
	F	$HgBr_2$, PhMe, MS, 70-72°, 50 h; rt, 15 h	(39)	1267
	F	C_6H_6, MeCN, 70-72°, 50 h	(35)	1267
	Cl	C_6H_6, MS, 70-72°, 50 h	(43)	1267
	Cl	C_6H_6, MeCN, 70°, 48 h	(37)	1267
	Br	$HgBr_2$, C_6H_6, MS, 70-72°, 50 h	(45)	1267
	Br	MeCN, C_6H_6, 70°, 48 h	(43)	1267
	I	$HgBr_2$, PhMe, C_6H_6, 70°, 48 h	(61)	1267
	NHAc	MeCN, MS, 50°, 4 d	(83)	1260
	CN	MeCN, MS, 70°, 95 h	(16)	1260
	CH_2OBn	MeCN, 70°, 2 d	(37) + α-anomer (8)	1268
		1. $Hg(CN)_2$, $MeNO_2$, reflux, 4 h 2. H_2S 3. NaOMe, MeOH	 (34)	1265

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, reflux, 25 min	 (26) + bis(riboside) (13) + N^3-isomer (19)	60
		MeCN, reflux, 8 h	 (59) R = 	254
		1. $HgBr_2$, C_6H_6, reflux, 2 h 2. 25°, 16 h	 (13) + *S* isomer (18)	1269
		1. $HgBr_2$, C_6H_6, reflux, 2 h 2. 25°, 16 h	 (—)	1269
		MeCN, MS, 100°, 4 h	 (41)	1260
		PhMe, reflux, 12 h	 (—)	1248
		C_6H_6, reflux, 1 h	 (—)	1248
		MeCN, reflux, time		60

R^1	R^2	R^3	time (min)	
NHAc	H	$Hg/_2$	80	(20)
OMe	Me	$Hg/_2$	7	(43)
OMe	H	HgCl	20	(26) + bis(riboside) (13)

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

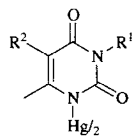
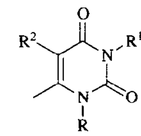
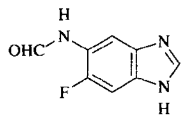
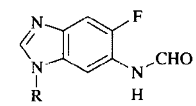
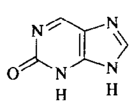
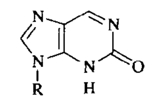
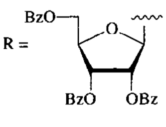
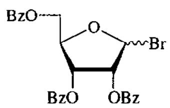
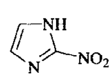
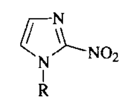
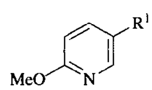
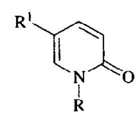
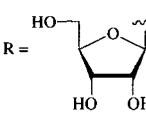
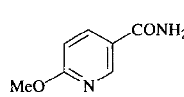
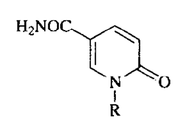
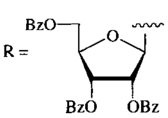
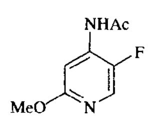
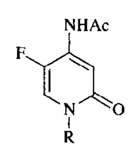
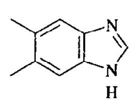
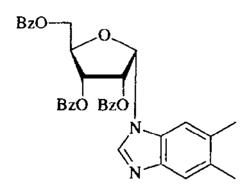
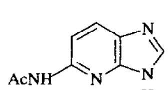
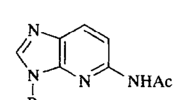
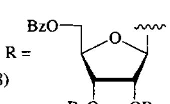
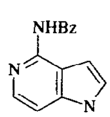
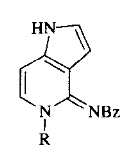
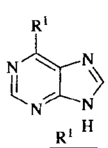
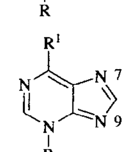
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, reflux	 R[1] / R[2]: H / Me, 2 h (13); Me / H, 2 h (69); Bn / H, 20 min (69)	60
		$Hg(CN)_2$, $MeNO_2$, MS, reflux, 4-8 h	 (38) + N^1-isomer (36)	1270
		$Hg(OAc)_2$, $HgBr_2$, PhMe, reflux, 22 h	 (36) R = 	1206
		$Hg(CN)_2$, MeCN, 60°, 2.5 h	 (68)	213
		1. MeCN, rt, 3 d 2. NH_3, MeOH	 R[1]: NHAc (61); NHCbz (52) R = 	1186
		DMF, rt, 3 d	 (63) R = 	1186
		MeCN, MS, rt, 4 d	 (38)	1226
		Dioxane, reflux, 2.5 h	 (28)	50
		$Hg(CN)_2$, MS, reflux, 3 h	 (72) + α-anomer (18) R = 	889
		$Hg(CN)_2$, MeCN, MS, 50°, 7.5 h	 (50)	1271
		MeCN		
	R[1] = NH_2	50°, 36 h	(25)	1243
		50°	(21)	1272
	R[1] = NMe_2	60-65°, 18 h	(46) + N^9-anomer (11)	61

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

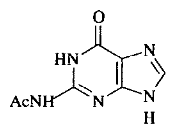
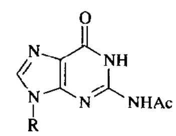
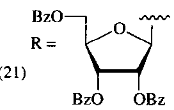
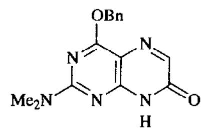
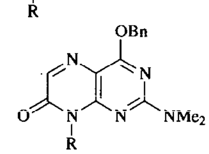
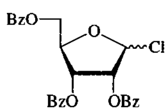
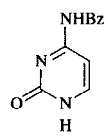
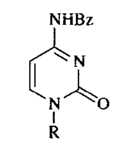
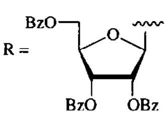
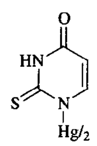
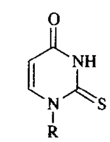
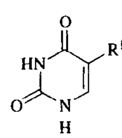
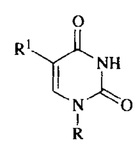
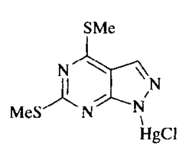
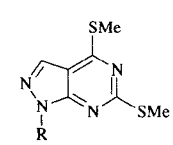
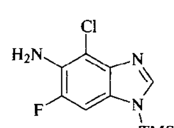
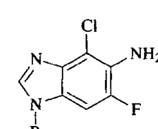
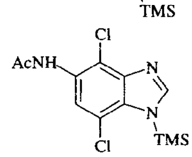
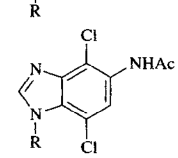
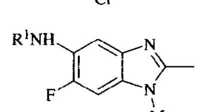
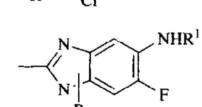
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		DMA, 60-65°, 40 h	 (19) + N^7-isomer (21) R = 	61
		$Hg(CN)_2$, $MeNO_2$, MS, 101°, 30 min	 **I** (76)	1112
		$EtNO_2$, MS, 114°, 30 min	**I** (75)	1112
		$Hg(CN)_2$, $MeNO_2$, reflux, 6 h	 (77) R = 	516
		Xylene, reflux, 1 h	 (—) + N^3-isomer (—) + N^1,N^3-bis(isomer) (—)	1273
		$Hg(CN)_2$, $MeNO_2$, reflux, 6 h		516
	R^1			
	H		(77)	
	F		(88)	
	CN		(70)	
	NO_2		(80)	
	Me		(85)	
	CO_2Et		(30)	
		PhMe, 140°, 4 h	 (60) + α-anomer (5)	1094
		$Hg(CN)_2$, $MeNO_2$, MS, reflux, 6-8 h	 (26) + N^3-isomer (19)	1270
		$Hg(CN)_2$, $MeNO_2$, MS, reflux, 4-8 h	 (22) + N^3-isomer (18)	1270
		$Hg(CN)_2$, $MeNO_2$, MS, reflux, 4-8 h	 R^1: H (3) N^1:N^3 = 74:26; CHO (5) N^1:N^3 = 64:36	1270

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

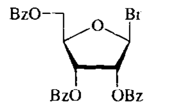
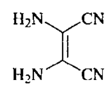
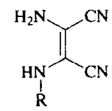
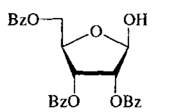
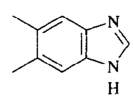
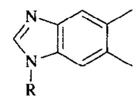
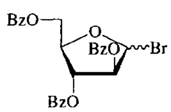
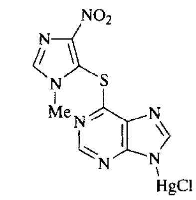
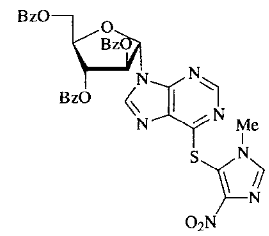
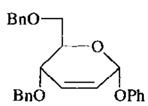
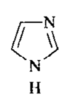
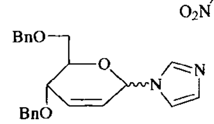
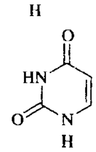
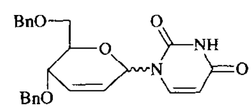
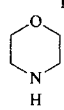
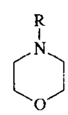
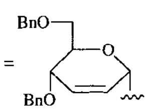
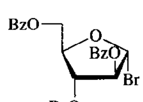
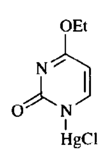
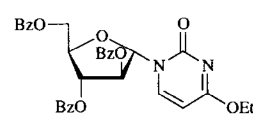
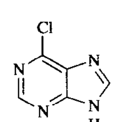
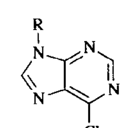
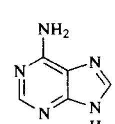
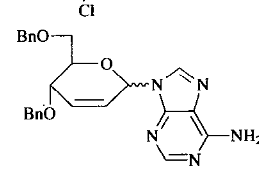
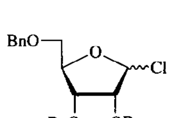
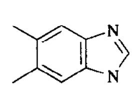
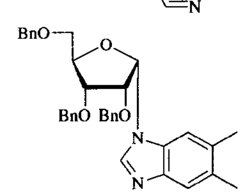
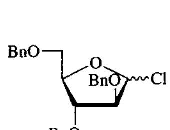
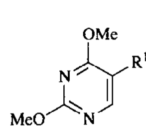
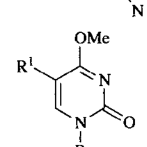
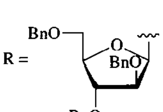
Sugar	Base	Conditions	Product(s) and Yield(s) (%)		Refs.
		Dioxane, rt, 24 h		(44)	161
		1. CETF, $Cl(CH_2)_2Cl$, Et_3N, $EtO_3^+ BF_4^-$ 2. DME, 60°, 10 h		(66)	429
		Xylene, reflux, 4 h		(—)	1193
		$Pd(dba)_3$, $[Ph_2PCH_2CH_2]_2$, THF, 60-70°		(72) α:β = 90:10	440
		$Pd(dba)_3$, $[Ph_2PCH_2CH_2]_2$, THF, 60-70°		(36) α:β = 90:10	440
		$Pd(dba)_3$, $[Ph_2PCH_2CH_2]_2$, THF, 60-70°		(85) R = 	440
		$HgBr_2$, xylene		(40)	1195
		$Pd(dba)_3$, $[Ph_2PCH_2CH_2]_2$, THF, 60-70°		(41)	440
		$Pd(dba)_3$, $[Ph_2PCH_2CH_2]_2$, THF, 60-70°		(80) α:β = 77:23	440
		Dioxane, 100°, 1.5 h		(66)	50
		CH_2Cl_2, rt, 3 d		R^1: H (—); CF_3 (100); R = 	356

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

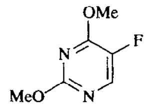
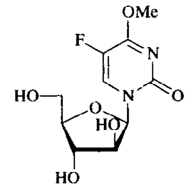
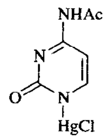
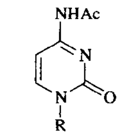
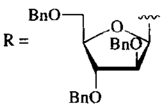
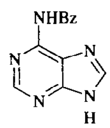
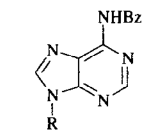
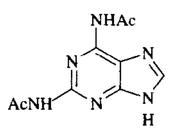
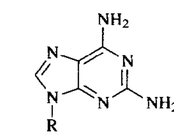
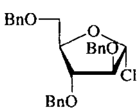
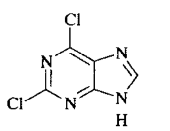
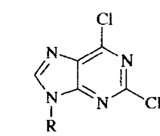
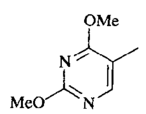
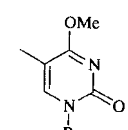
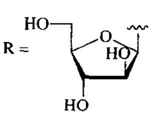
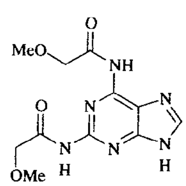
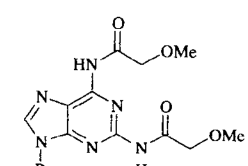
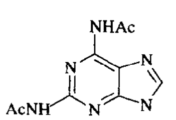
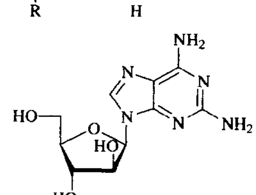
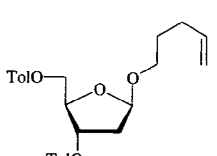
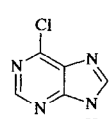
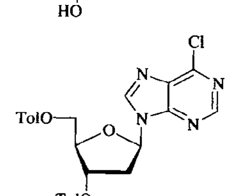
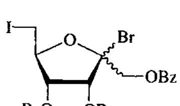
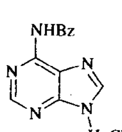
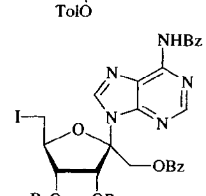
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CH_2Cl_2, MS, rt, 3 d 2. H_2, $PdCl_2$, MeOH, 15 min	 (25)	1274
		PhMe, reflux, 30 min	 (—) R = 	356
		CH_2Cl_2, MS, rt, 1 week	 (46)	341
		1. $Cl(CH_2)_2Cl$, MS, reflux 2. $MeNH_2$, EtOH, 55-60°, 18-42 h	 (41)	345
		1. CH_2Cl_2, MS, rt, 1 week 2. NH_3, MeOH. 0°	 I (28)	342
		$Hg(CN)_2$, $MeNO_2$, reflux, 3 h	I (11) + α-anomer (25)	343
		1. CH_2Cl_2, rt, 5 d 2. H_2, $PdCl_2$	 (49) R = 	357
		$Cl(CH_2)_2Cl$, reflux, 10 h	 (100)	347
		1. $Cl(CH_2)_2Cl$, reflux, 5 d 2. NaOMe, MeOH	 (40)	344
		IDCP, MeCN, MS, rt, 2 h	 (35) + α-anomer (17) + N^7-(α,β)-isomer (39)	421
C_{27} 		$MeNO_2$, rt, 48 h	 (49)	632

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

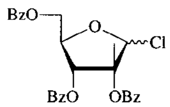
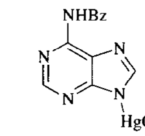
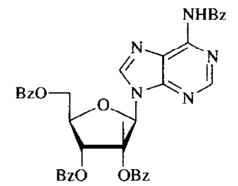
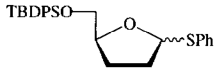
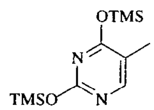
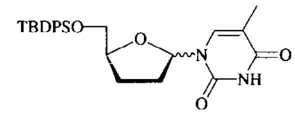
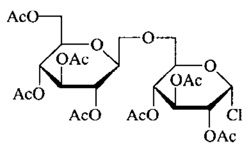
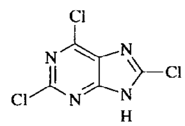
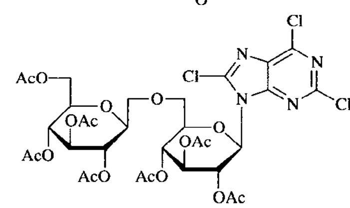
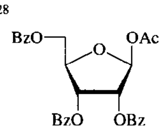
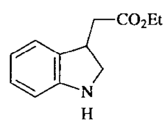
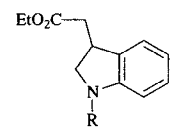
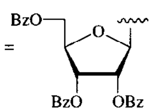
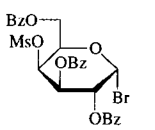
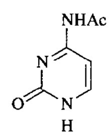
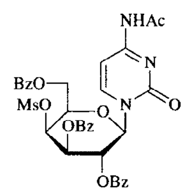
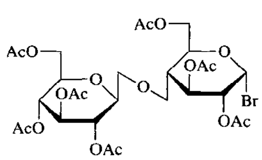
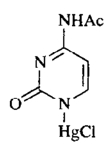
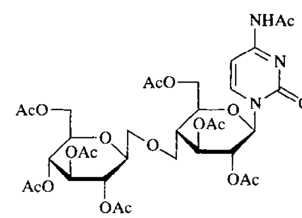
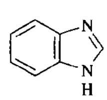
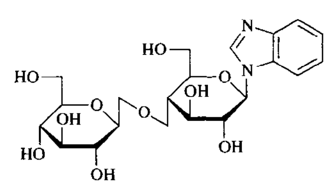
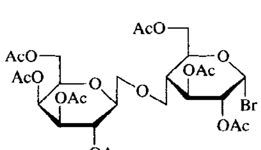
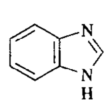
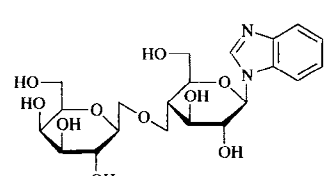
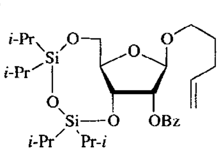
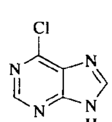
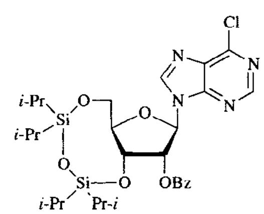
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		Xylene, 145°, 1.3 h	 (—)	1275
		NBS, CH_2Cl_2, MS, rt, 5 min	 (94) α:β = 6:1	406
		$Hg(CN)_2$, $MeNO_2$, reflux, 3 h	 (45)	1247
C_{28}				
		HOAc (100%), EtOH, reflux, 5 h	 (92) R = 	1276
		$Hg(CN)_2$, $MeNO_2$, CH_2Cl_2, reflux, 3.5 h	 (96)	517
		C_6H_6, reflux, 14 h	 (24)	1231
		1. $Hg(CN)_2$, $MeNO_2$, MS, reflux, 18 h 2. NaOMe, MeOH	 (26)	1277
		1. $Hg(CN)_2$, $MeNO_2$, MS, reflux, 18 h 2. NaOMe, MeOH	 (—)	1277
C_{29}				
		NIS, TfOH, MeCN, MS, rt, 2 h	 (60) + N^7-isomer (10)	421

TABLE X. MISCELLANEOUS REACTIONS OF HETEROCYCLIC BASES WITH PROTECTED SUGARS (*Continued*)

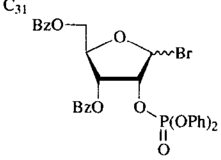
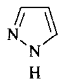
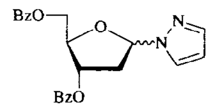
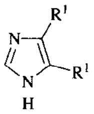
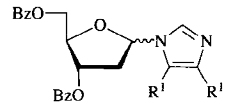
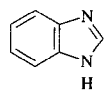
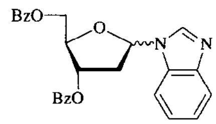
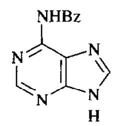
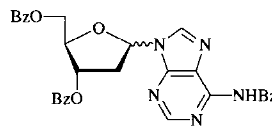
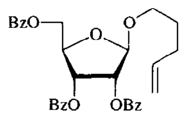
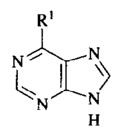
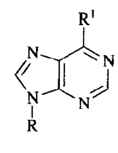
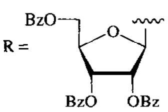
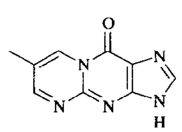
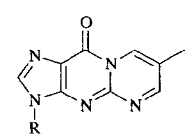
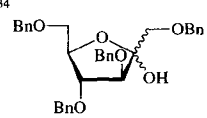
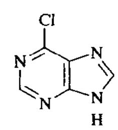
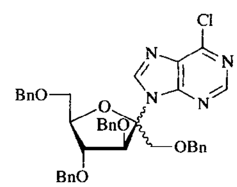
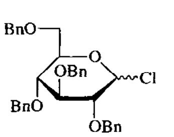
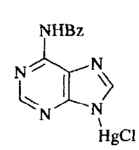
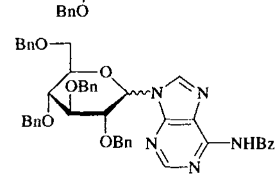
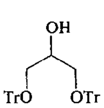
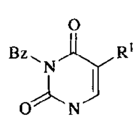
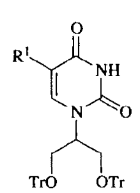
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{31} 		Bu_3SnH, $h\nu$	 (82) $\alpha:\beta = 1.4:1$	434
	 R^1: H, Cl, Ph	Bu_3SnH, $h\nu$	 (60) $\alpha:\beta = 1:1$; (66) $\alpha:\beta = 2.4:1$; (54) $\alpha:\beta = 1.8:1$	434
		Bu_3SnH, $h\nu$	 (47) $\alpha:\beta = 1.5:1$	434
		Bu_3SnH, $h\nu$	 (42) $\alpha:\beta = 1:1$	434
		NIS, TfOH, MeCN, MS, rt, 40 min	 R = 	421
	R^1: Cl		(53)	
	NHMe		(65)	
	NHC_6H_{13}-*n*		(70)	
	NHBz		(50)	
		NIS, TfOH, MeCN, MS, rt, 40 min	 (60)	421
C_{34} 		Ph_3P, DEAD, THF, rt, 12 h	 (37) + α-anomer (12)	432
		$CdCO_3$, xylene	 (59) $\alpha:\beta = 1:1$	1071
		1. PPh_3, DEAD, dioxane, rt, 20 h 2. $MeNH_2$, EtOH	 R^1: H (88); Me (85)	1261

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES

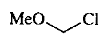
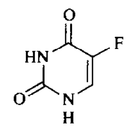
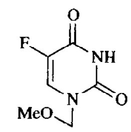
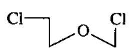
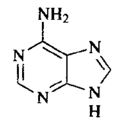
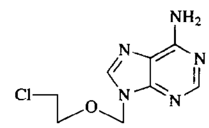
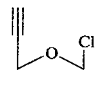
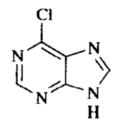
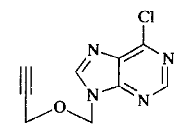
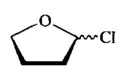
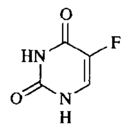
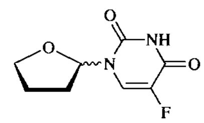
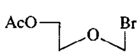
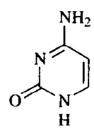
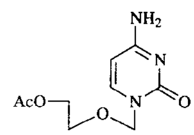
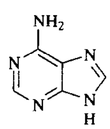
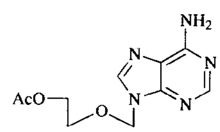
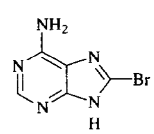
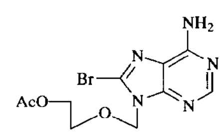
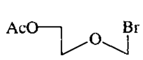
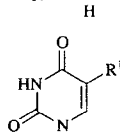
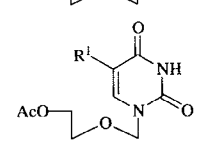
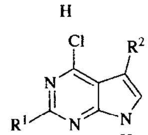
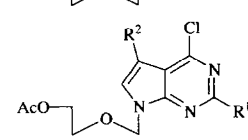
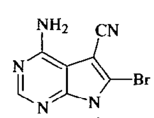
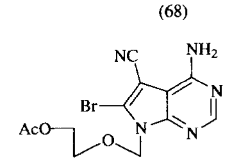
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
		K_2CO_3, CH_3CONMe_2, 30°, 5 h	 (11) + N^3-isomer (9) + N^1,N^3-bis(isomer) (19)	638
C_3				
		LiH, DMF	 (—)	1278
C_4				
		NaH, MeCN, 65°, 12 h	 (59) + N^7-isomer (6)	1279
		K_2CO_3, DMA, 30°, 5 h	 (75)	638
C_5				
		18-crown-6 or tetraglyme, THF, KOBu-*t*, 45 min	 0° (50) 25° (40) + N^3-isomer (20)	1280
		18-crown-6 or tetraglyme, THF, KOBu-*t*, 45 min	 0° (50) 25° (31) + N^9-isomer (19)	1280
		18-crown-6 or tetraglyme, THF, KOBu-*t*, 45 min	 0° (50) 25° (41) + N^9-isomer (27)	1280
		18-crown-6 or tetraglyme, THF, KOBu-*t*, 45 min	 R^1 / 0° / 25° / N^3-isomer H / (50) / (34) / (17) Me / (60) / (33) / (16)	1280
				
	R^1 / R^2			
	H / H	NaH, DMF, rt, 3 h	(40)	1281
	H / Cl	NaH, DMF, rt, 30 min	(51)	1281
	Cl / H	NaH, DMF, rt, 2 h	(50)	1282
	H / Br	NaH, DMF, rt, 45 min	(45)	1281
	NH_2 / H	NaOH (50%), Bu_4NHSO_4, C_6H_6, rt, 1 min	(50)	1282
	AcNH / H	NaH, DMF, rt, 5 h	(42)	1282
	SMe / H	NaH, DMF, rt, 1 h	(68)	1282
		NaH, DMF, 100°, 6 h	 (65) + N^7 & N^1-isomers (—)	1283

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

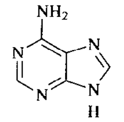
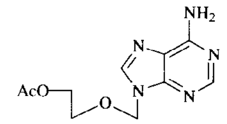
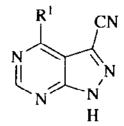
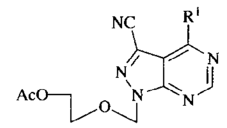
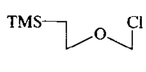
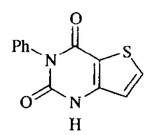
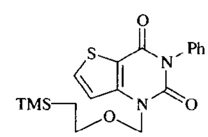
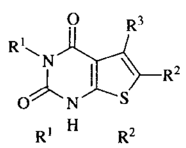
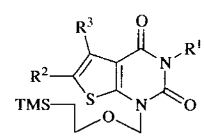
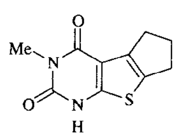
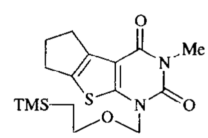
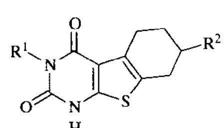
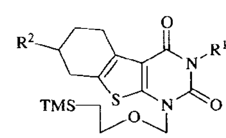
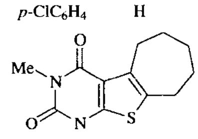
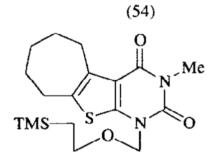
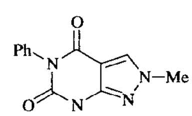
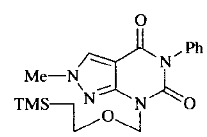
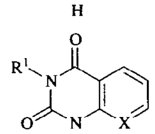
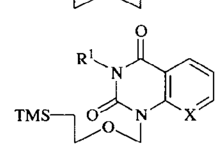
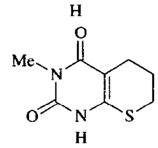
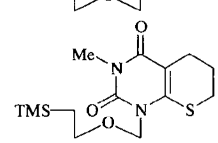
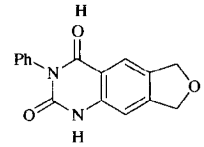
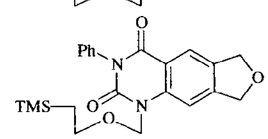
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		NaH, MeCN, rt, 2 h	 (75)	1284
		NaH, DMF, 78°	 R^1: NH_2 4 h (41); NHAc 2 h (—)	1285
C_6 		NaH, DMF, rt, 12 h	 (88)	894
	 R^1 / R^2 / R^3: Me / H / H Me / Et / H Ph / Ph / H Me / Me / Me	NaH, DMF, rt, 12 h	 (17) (19) (57) (43)	894
		NaH, DMF, rt, 12 h	 (50)	894
	 R^1 / R^2: Me / H Ph / Me p-ClC_6H_4 / H	NaH, DMF, rt, 12 h	 (50) (63) (54)	894
		NaH, DMF, rt, 12 h	 (66)	894
		NaH, DMF, rt, 12 h	 (52)	894
		NaH, DMF, rt, 12 h	 R^1 / X: Me / CH (36); Ph / N (36)	894
		NaH, DMF, rt, 12 h	 (25)	894
		NaH, DMF, rt, 12 h	 (42)	894

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

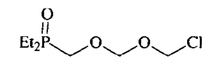
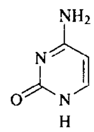
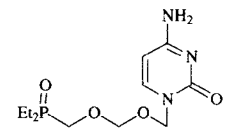
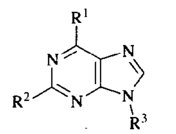
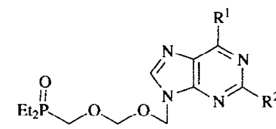
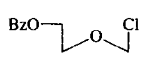
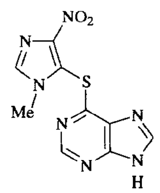
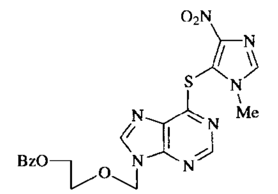
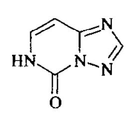
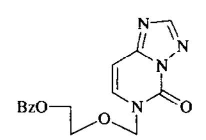
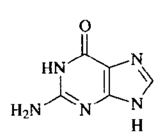
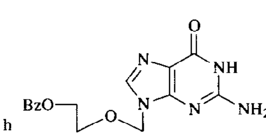
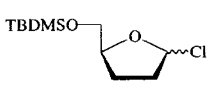
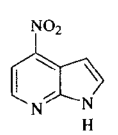
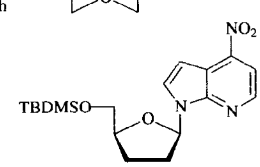
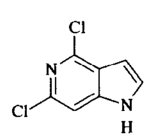
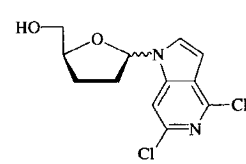
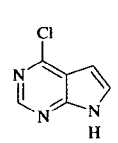
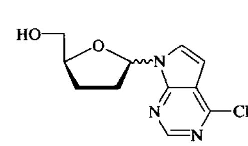
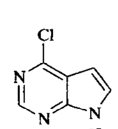
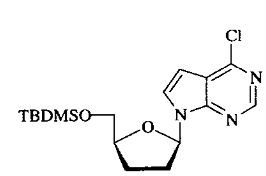
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		NaH, DMF, rt, 15 h	 (22)	650
		NaH, DMF, 25°, 15 h		
	R^1 / R^2 / R^3			
	NH_2 / H / H		(50)	650
	Cl / NH_2 / H		(23)	650
	NH_2 / H / Na		(—)	977
	Cl / NH_2 / Na		(—)	977
C_{10} 		Et_3N, DMF, rt, 4 h	 I (86)	1092
		1. Et_3N, DMF, 10-15° 2. rt, 4 h	I (86)	1092
		Et_3N, DMF, rt, 18 h	 (60)	743
		1. HMDS, $(NH_4)_2SO_4$ 2. Bu_4NF, THF, C_6H_6, reflux, 3 h 3. $BzO(CH_2)_2OCl$, reflux, 3 h	 (92)	1113
C_{11} 		K_2CO_3, TDA-1, MeCN, rt, 1 h	 (17) + α-anomer (71)	1286
		1. KOH, TDA-1, MeCN, rt 2. Bu_4NF, THF	 (55) α:β = 1:1	1287
		1. KOH, TDA-1, MeCN, rt 2. Bu_4NF, THF	 (55) α:β = 1:1	1287
		KOH, TDA-1, MeCN, rt	 (46) + α-anomer (18)	1288

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

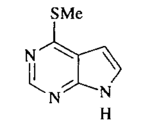
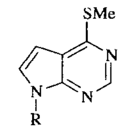
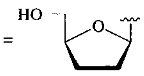
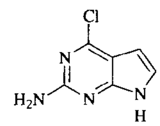
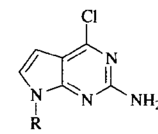
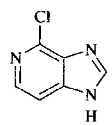
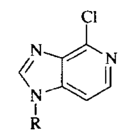
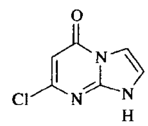
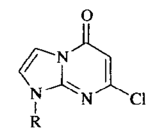
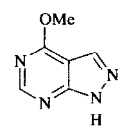
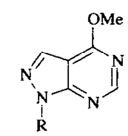
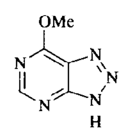
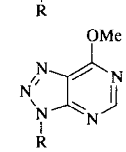
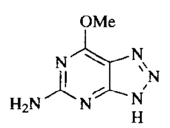
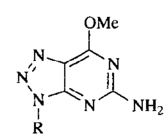
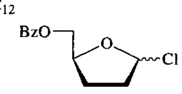
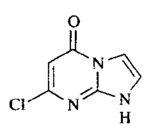
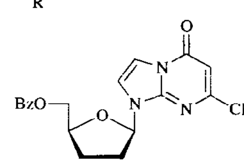
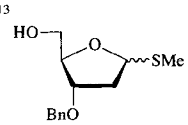
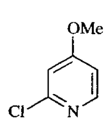
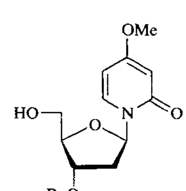
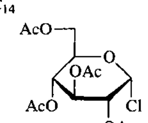
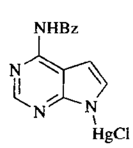
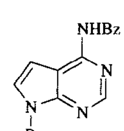
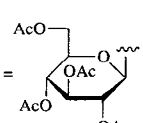
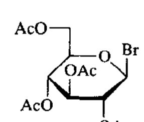
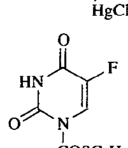
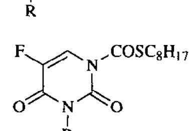
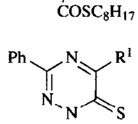
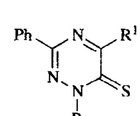
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. KOH, TDA-1, MeCN, rt 2. Bu_4NF, THF	 (57) R = 	1287
		KOH, TDA-1, MeCN, rt, 10 min	 (22) + α-anomer (20)	1288
		KOH, TDA-1, MeCN, rt, 10 min	 (22) + α-anomer (26) + N^3-β-isomer (17) + N^3-α-isomer (13)	1289
		K_2CO_3, TDA-1, MeCN	 (46) + α-anomer (35)	1290, 1291
		KOH, TDA-1, MeCN	 (22) + α-anomer (18) + N^8-β-isomer (9) + N^8-α-isomer (9)	1292
		KOH, TDA-1, MeCN	 (—)	1291
		KOH, TDA-1, MeCN	 (14) + N^3-isomer (12) + N^2-isomer (21) + N^1-isomer (5)	1293
C_{12} 		K_2CO_3, TDA-1, MeCN, rt, 50 min	 (45) + α-anomer (43)	1290
C_{13} 		1. NaH, DMF, 80°, 2 h 2. $Me_2S(SMe)BF_4$, CH_2Cl_2, MS, rt or −20°, 4 h 3. OH^-	 (—)	97
C_{14} 		$CdCO_3$, xylene, reflux, 24 h	 (47) R = 	1071
		$(i\text{-}Pr)_2NEt$, DMF, rt, 12 h	 (75)	1294
		KOH, Me_2CO, H_2O, rt, 12 h	 R^1: Bn (64); $CH_2C_6H_4OMe$-*p* (73); $CH_2C_6H_4Cl$-*p* (10)	1295

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

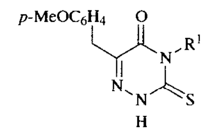
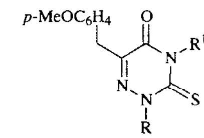
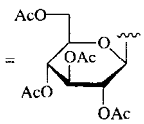
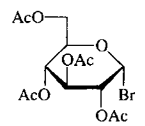
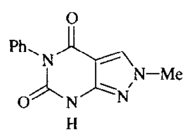
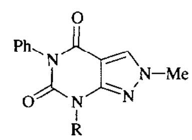
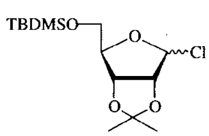
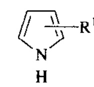
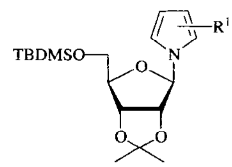
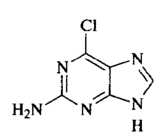
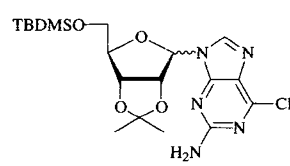
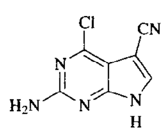
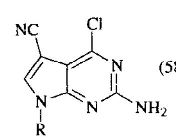
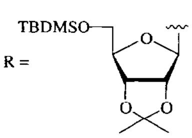
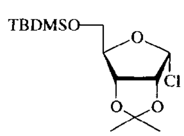
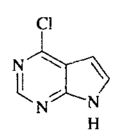
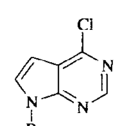
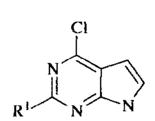
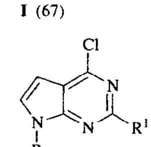
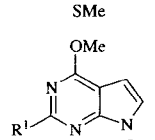
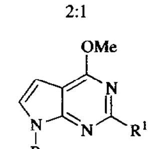
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		KOH, Me_2CO, H_2O, rt, 12 h	 R = 	1295
	R^1			
	Ph		(82)	
	p-$MeOC_6H_4$		(57)	
	p-MeC_6H_4		(78)	
		NaH, DMF, rt, 12 h	 (17)	894
		NaH, MeCN, rt	 R^1	
			2-CN 12 h (61)	68
			3-CN 15 h (66)	1296, 1297
		K_2CO_3, NMP, 80°, 3 h	 **I** (23) α:β = 2.5:1	1298
		Cs_2CO_3, NMP, 55°, 3 h	**I** (25-38) α:β = 7.7:1	1298
		NaH, MeCN, rt, 12 h	 (58) R = 	1299
		KOH, TDA-1, MeCN, rt, 10 min	 **I** (65)	1300
		NaH, MeCN, rt, 30 min	**I** (67)	1297
		KOH, TDA-1, MeCN, rt, 20 h		
	R^1		Base:Sugar	
	NH_2		1:1 (34)	1301
	NH_2		2:1 (65)	1301
	SMe		1:1 (53)	1301
	SMe		2:1 (78)	1301
		KOH, TDA-1, MeCN, rt, 20 h		
	R^1		Base:Sugar	
	NH_2		1:1 (21)	1301
	NH_2		2:1 (31)	1301
	SMe		1:1 (59)	1301
	SMe		2:1 (82)	1301

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

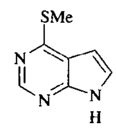
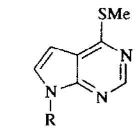
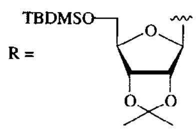
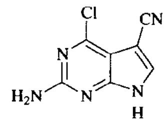
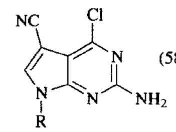
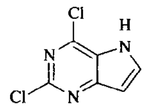
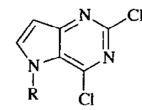
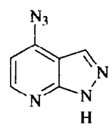
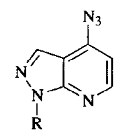
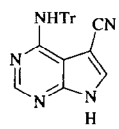
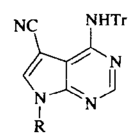
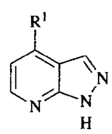
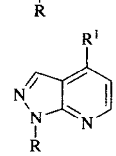
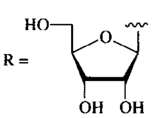
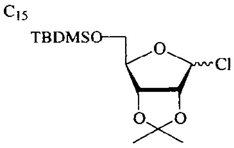
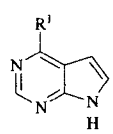
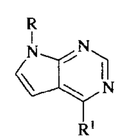
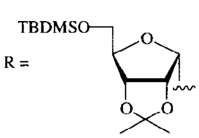
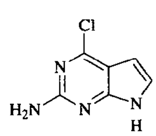
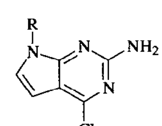
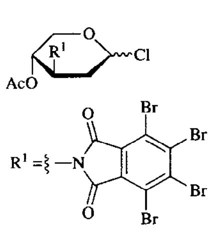
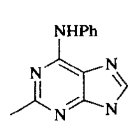
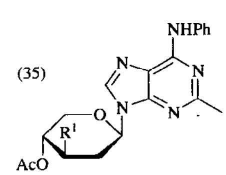
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		KOH, TDA-1, MeCN, rt, 10 min	 (65) R = 	1300
		NaH, MeCN, rt, 12 h	 (58)	1297
		NaH, MeCN, rt, 24 h	 (63) + α-anomer (13)	1302
		NaH, MeCN, rt, 12 h	 (50)	1303
		NaH, MeCN, MS, 50°, 17 h	 (>62)	580
		1. NaH, MeCN, rt, 12 h 2. TFA, H_2O	 R = 	1303
	R^1			
	Cl		(39)	
	OMe		(40)	
	H		(35)	
C_{15} 		KOH, TDA-1, MeCN, rt, 10 min	 R = 	1300
	R^1			
	Cl		(46)	
	SMe		(45)	
		KOH, TDA-1, MeCN, rt, 20 h	 Base:Sugar 1:1 (31); β-anomer (11)	1301
		NaH, MeCN	Base:Sugar 1:1 (—); β-anomer (53)	1304
		NaH, MeCN, rt, 18 h	(35) 	1305

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

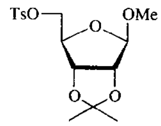
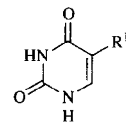
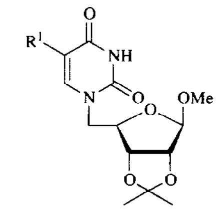
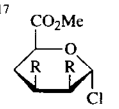
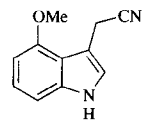
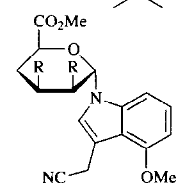
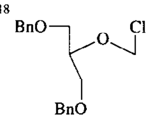
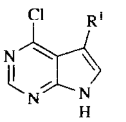
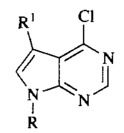
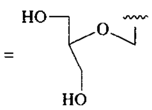
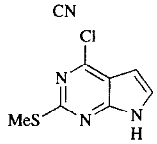
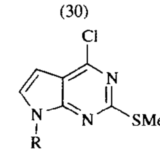
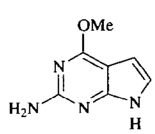
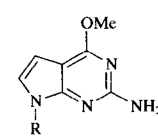
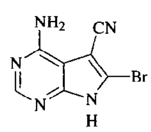
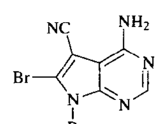
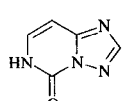
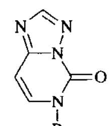
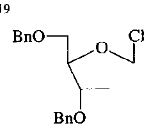
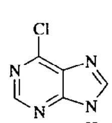
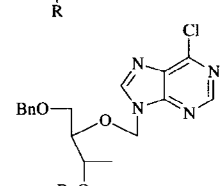
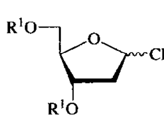
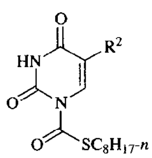
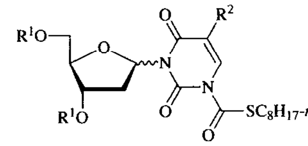
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 		NaH, DMF	 R^1: H (37); I (58)	1033
C_{17}  R = OPiv		NaH, MeCN, 0°	 (44)	1306, 1307
C_{18} 		1. NaH, DMF, rt, 40 min 2. BCl_3, CH_2Cl_2, −78°, 15 min	 R = 	
	R^1			
	H		(39)	1308
	Cl		(34)	1308
	Br		(41)	1308
	I		(38)	1308
	Me		(44)	1308
	CN		(30)	1309
		NaH, DMF, rt, 20 h	 (75)	1309
		NaOH (50%), CH_2Cl_2, rt, 25 min	 (27)	838
		NaH, DMF, 80°, 5 h	 (55)	1309
		Et_3N, DMF, rt, 18 h	 (56)	743
C_{19} 		NaH, MeCN	 (—) + N^7-isomer (—)	1310
 R^1 = p-ClC_6H_4CO		(i-Pr)$_2$NEt, MeCN, rt, 12 h		256a
	R^2			
	H		(82) α:β = 48:52	
	F		(100) α:β = 60:40	
	Me		(87) α:β = 45:55	

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

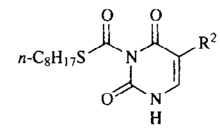
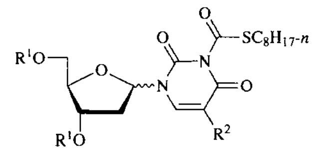
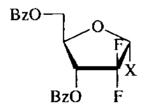
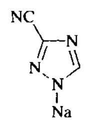
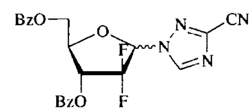
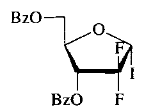
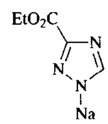
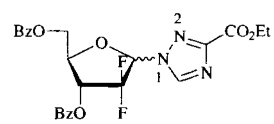
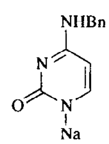
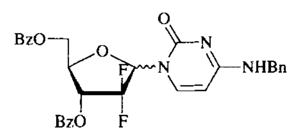
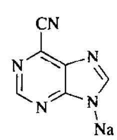
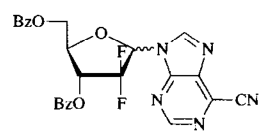
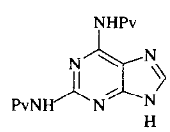
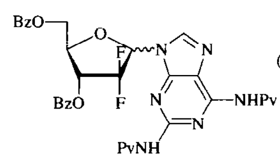
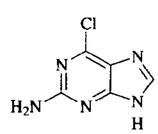
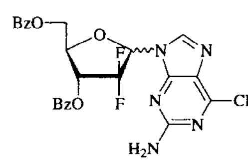
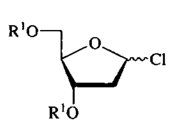
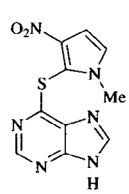
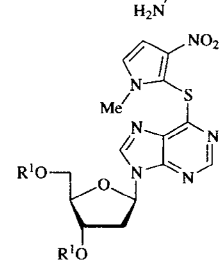
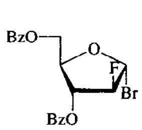
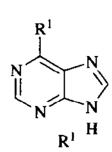
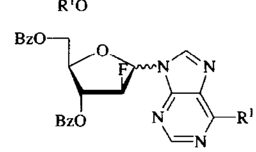
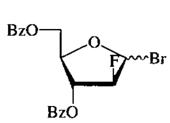
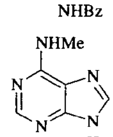
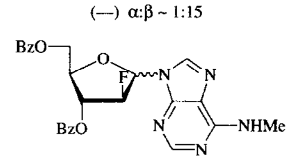
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$(i\text{-Pr})_2NEt$, MeCN, rt, 12 h	 R^2: H (75); F (86); Me (76)	256a
		MeCN, 82°		1311
	X: Br	78 h	(6) α:β = 1:1.2	
	X: I	48 h	(48) α:β = 1:3.5	
		DMA, 23°, 24 h	 (67) α:β = 1:3; N^1:N^2 = 13:41.5	1311
		DMA, 23°, 5 h	 (7) α:β = 1:1.9	1311
		DMA, 70°, 5 h	 (7) α:β = 1:1.2	1311
		KOBu-*t*, MeCN, 60°, 16 h	 (25) α:β = 1:2.2	1311
		KOH, DMA, 70°, 5 h	 (—) α:β = 1:3	1311
 R^1 = p-$O_2NC_6H_4CO$		NaH, MeCN, rt, 15 h	 (55)	1092
		NaH, mineral oil		393
	R^1: Cl	55°, 3 h	(73) α:β = 1:10	
	R^1: NHBz	reflux, 3 h	(—) α:β ~ 1:15	
		NaH, DMF, rt, 12 h	 (62)	298

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

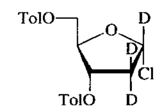
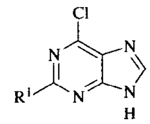
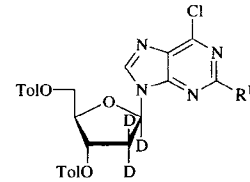
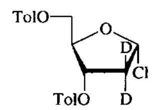
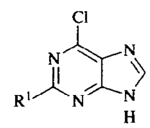
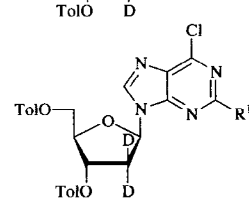
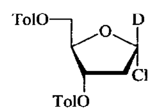
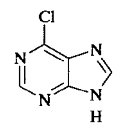
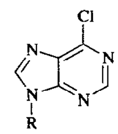
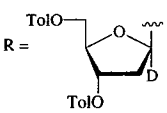
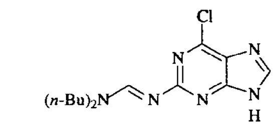
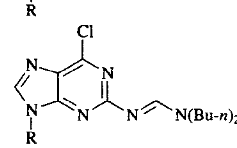
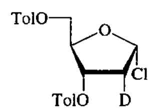
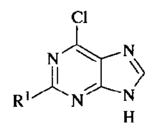
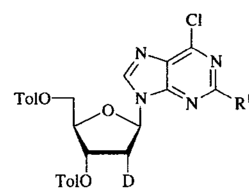
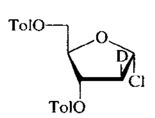
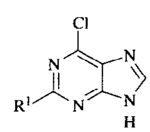
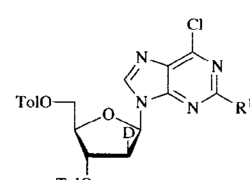
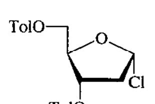
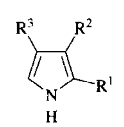
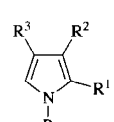
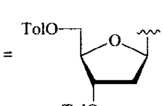
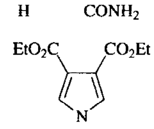
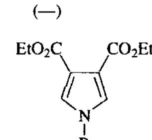
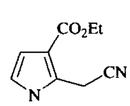
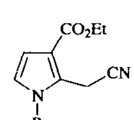
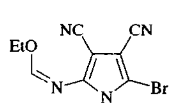
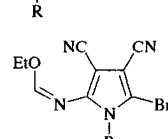
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21} 		NaH, MeCN, rt	 R^1 Cl 4 h (60) NH_2 20 h (61)	1312
		NaH, MeCN, rt, 20 h	 R^1 H (48) NH_2 (51)	1313
		NaH, MeCN, rt, 4 h	 (53) R = 	1312
		1. NaH, MeCN, rt, 10 min 2. Pyridine-2-carbaldoxime, rt, 2 h	 (26) + N^7-isomer (—) + N^3-isomer (—) + N^3,N^7-bis(isomer) (—)	1312
		NaH, MeCN, rt, 20 h	 R^1 H (56) NH_2 (57)	1314
		NaH, MeCN, rt, 24 h	 R^1 H (54) NH_2 (52)	1314
		NaH, MeCN, rt	 R = 	
	R^1 R^2 R^3			
	CN H H		(67)	1315
	H CN H		(65)	1297
	CN H CN		(68)	1315
	H $CONH_2$ CO_2Me		(—)	1315
		NaH, MeCN, rt, 0.5 h; 50°, 1 h	 (70)	1316
		NaH, MeCN, rt	 (95)	1317, 1318
		NaH, MeCN, rt, 0.5 h; 50°, 1 h	 (75)	1316

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

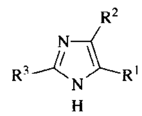
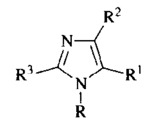
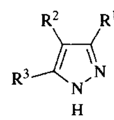
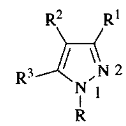
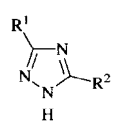
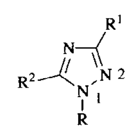
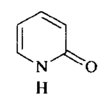
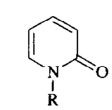
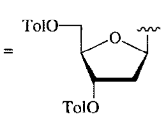
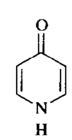
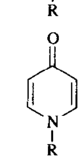
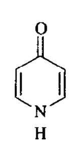
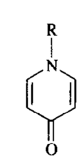
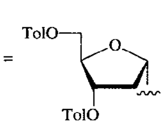
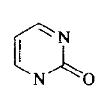
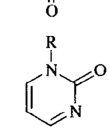
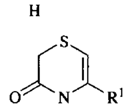
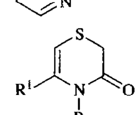
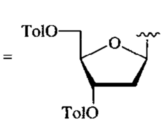
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
				
	R^1, R^2, R^3			
	H, Ph, H	NaH, MeCN, rt, 3 h	(53)	1319
	H, m-$O_2NC_6H_4$, H	NaH, MeCN, rt, 3 h	(65)	1319
	NH_2, CN, H	NaH, MeCN, rt, 15 min	(45) + N^3-isomer (21)	1320
	NH_2, CO_2Et, H	NaH, MeCN, rt, 3 h	(10) + N^3-α-isomer (1) + N^3-β-isomer (28)	1321
	CH_2CN, CO_2Me, H	NaH, MeCN, rt, 30 min	(49) + N^3-isomer (45)	1297
	CH_2CN, CO_2Me, H	NaH, MeCN, rt, 3 h	(48) + N^3-β-isomer (45)	1322
	$CH(OEt)_2$, CO_2Me, H	NaH, MeCN, rt, 2 h	(70)	1323
	Ac, H, ONa	DME, rt, 40 h	(43) α:β = 1:1.7	929
	CO_2Me, CH_2CN, Cl	NaH, MeCN, rt, 3 h	(65)	1324
	CO_2Me, CH_2CN, SMe	NaH, MeCN, rt, 3 h	(68)	1324
				
	R^1, R^2, R^3			
	CH_2CN, CO_2Me, H	NaH, MeCN, rt, 4 h	(38) + N^2-isomer (18)	1325
	SMe, CN, NH_2	NaH, MeCN, rt, 20 min	(47) + N^2-isomer (34)	1326
				
	R^1, R^2			
	CN, H	NaH, MeCN, rt, 30 min	(35)	1327
	CO_2Me, H	NaH, MeCN, rt, 30 min	(28)	1327
	SO_2NH_2, H	NaH, MeCN, rt, 20 h	(40) + N^2-isomer (13)	1328
	NO_2, Br	NaH, MeCN, rt, 12 h	(63)	1329
		1. KOH, MeCN 2. TsOH, rt, 48 h	 (33) + α-anomer (22) R = 	1330
		1. KOH, MeCN 2. H^+, 60°, 10 min	 (41) + α-anomer (42)	1330
		1. KOH, MeCN 2. H^+, rt, 10 min	 (—) R = 	1330
		LiOH, MeCN, 60°, 30 min	 (64)	1330
		NaH, MeCN, rt	 R = 	1331
	R^1			
	H	3 h	(79)	
	Me	30 min	(38)	
	CO_2Et	3 h	(35)	

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

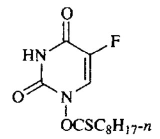
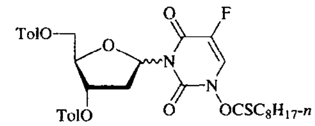
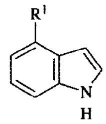
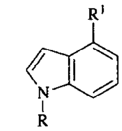
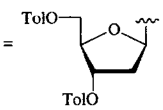
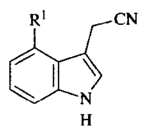
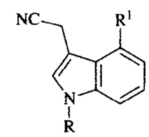
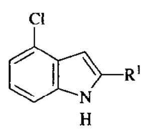
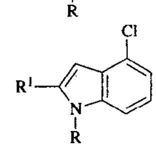
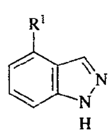
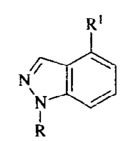
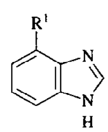
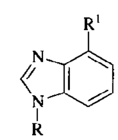
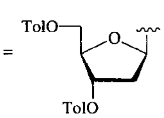
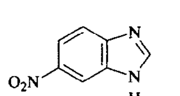
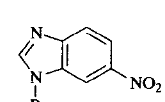
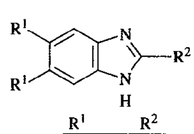
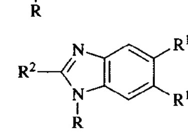
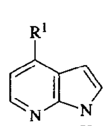
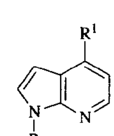
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		$(i\text{-Pr})_2NEt$, THF or DMF, rt, 12 h	 (100)	256a
		NaH, MeCN	 R = 	
	R^1			
	H	rt, 12 h	(75)	1332
	NO_2	rt, 12 h	(82)	1332
	CN	rt, 12 h	(79)	1332
	CO_2Me	0-25°	(86)	1333
		NaH, MeCN, rt	 R^1: H, 12 h (70); OMe, 30 min (90)	1332; 1297, 1332
		NaH, MeCN, rt, 12 h	 R^1: CN (57); $CONH_2$ (60)	1332
		KOH, TDA-1, MeCN, rt, 20 min	 R^1: H (34) + N^2-isomer (21); NO_2 (34) + N^2-isomer (34)	1334
		KOH, MeCN	 R = 	
	R^1			
	H	rt, 15 min	(86)	1335
	NO_2	TDA-1, rt, 30 min	(45) + N^3-β-isomer (30) + N^3-α-isomer (6)	1336
	NO_2	18-crown-6, rt, 30 min	(49) + N^3-β-isomer (32) + N^3-α-isomer (8)	1336
	NO_2	K_2CO_3, TDA-1, MeCN, rt, 2 h	(12) + α-anomer (26)	1336
	NO_2	K_2CO_3, 18-crown-6, MeCN, rt, 2 h	(14) + α-anomer (27)	1336
		KOH, TDA-1, MeCN, rt, 2 h	 (39) + N^3-isomer (46)	1336
		NaH, MeCN, rt, 15 min		1335
	R^1 / R^2			
	F / H		(91)	
	Cl / H		(84)	
	Cl / CF_3		(57)	
	Cl / Me		(72)	
	Cl / Pr-*i*		(49)	
		KOH, TDA-1, MeCN, rt, 20 min	 R^1: H (55); NO_2 (78)	67, 1337

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

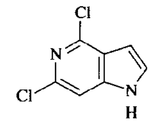
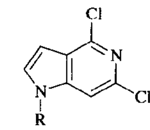
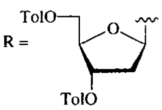
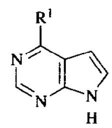
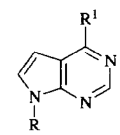
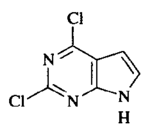
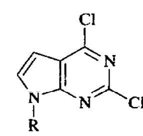
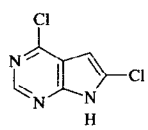
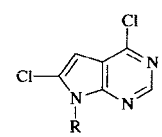
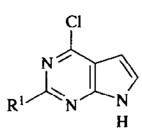
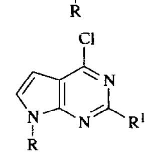
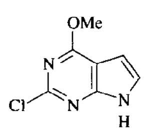
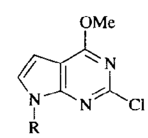
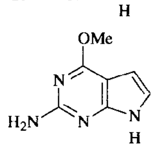
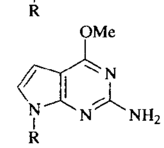
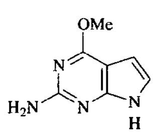
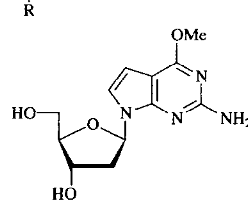
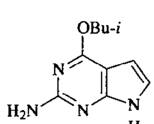
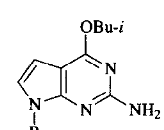
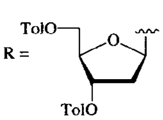
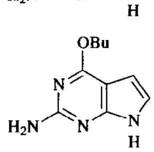
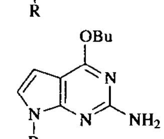
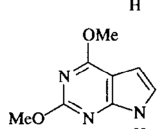
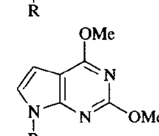
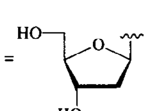
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		KOH, TDA-1, MeCN, rt, 15 min	 (90) R = 	1338
		KOH, TDA-1, MeCN, rt		
	R^1			
	Cl	15 min	(81)	1339
	NHMe	10 min	(66)	1340
	SMe	10 min	(80)	1340
		KOH, TDA-1, MeCN, rt, 15 min	 (61)	1341
		NaH, MeCN, rt, 12 h	 (63) + N^1-isomer (19)	1342
		NaH, MeCN, rt, 2 h	 R^1: NH_2 (78)	1343
			SMe (66)	64
		KOH, Bu_4NHSO_4, MeCN	NH_2 (46)	1344
		NaOH (50%), TEBA, CH_2Cl_2, $CHCl_3$, rt, 5 min	 (67) + α-anomer (7)	1345
		KOH, TDA-1, MeCN, rt, 5 min	 (61)	1346, 262
		1. KOH, Bu_4NHSO_4, CH_2Cl_2, rt, 3 min 2. NaOMe, MeOH, rt, 3 h	 (63)	1339, 1186
		NaOH, CH_2Cl_2, rt, 3 min	 (54) R = 	262
		KOH, TDA-1, MeCN, rt, 5 min	 (73)	262
		1. NaOH (50%), TEBA, CH_2Cl_2, $CHCl_3$, rt, 30 min 2. NaOMe, MeOH	 (67) R = 	1345

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

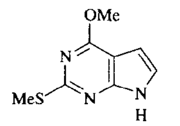
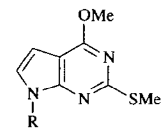
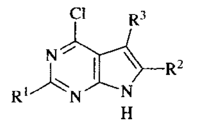
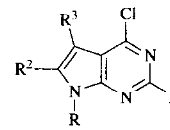
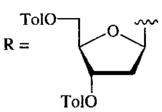
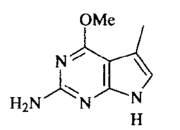
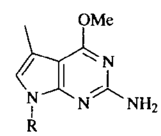
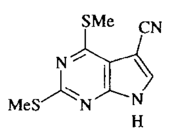
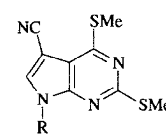
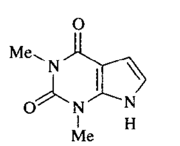
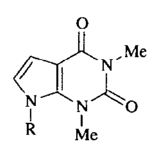
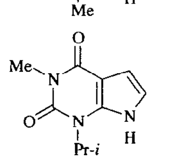
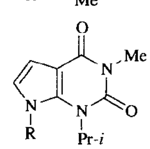
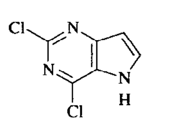
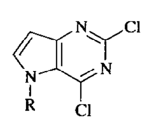
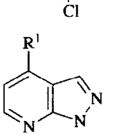
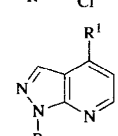
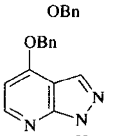
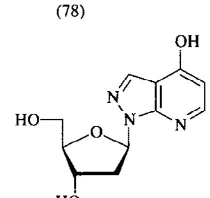
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. NaH, MeCN, rt, 45 min 2. Rexyn™ 201, MeOH, rt, 1.5 h	 (58)	1347
		NaH, MeCN, rt	 R = 	
	R^1 / R^2 / R^3			
	Me / Cl / H	12 h	(59)	1342
	SMe / Cl / H	30 min	(87)	1342
	H / Br / CN	2 h	(53)	1348
	NH_2 / H / CN	—	(75)	1349
	NH_2 / H / CO_2Me	30 min	(87)	1297
	SMe / Me / H	30 min	(80)	1342
		NaOH (50%), TEBA, CH_2Cl_2, rt, 5 min	 (47) + α-anomer (40)	1350
		NaH, MeCN, 50°, 2 h	 (72)	1351
		NaOH (50%), TEBA, CH_2Cl_2, rt	 (50) + α-anomer (21)	1352
		KOH, TDA-1, MeCN, rt, 15 min	 (42) + α-anomer (14)	1352
		NaH, MeCN, rt, 30 min	 (84)	1297 1353
		NaH, MeCN, rt		
	R^1			
	H	2 h	(95)	1303
	Cl	30 min	(63)	1297
	N_3	2 h	(61)	1303
	OMe	2 h	(64)	1303
	OBn	2 h	(78)	1303
		1. NaH, MeCN 2. NH_3, MeOH 3. H_2, Pd/C	 (60)	1354

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

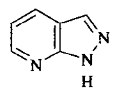
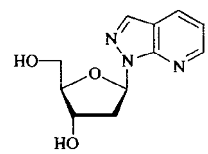
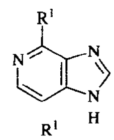
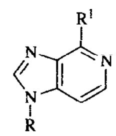
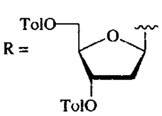
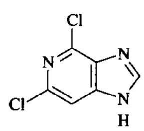
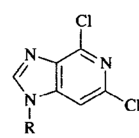
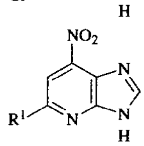
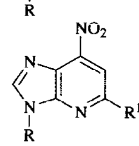
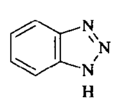
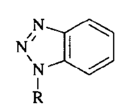
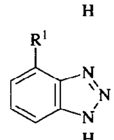
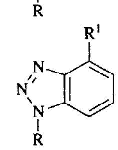
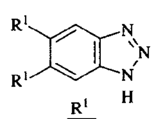
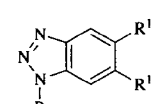
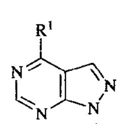
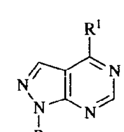
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. NaH, MeCN 2. NH_3, MeOH	 (—)	1354
		KOH, TDA-1, MeCN, rt	 R = 	
	R^1			
	Cl	1 h	(61) + N^3-isomer (26)	1355
	SMe	15 min	(68) + N^3-isomer (29)	1356
		NaH, MeCN, rt, 30 min	 (66)	1297, 64
		NaH, MeCN, 0°, 3 h	 R^1: H (60); Cl (50)	1357
		KOH, TDA-1, MeCN, rt, 15 min	 (57) + N^2-isomer (30)	271
		NaH, MeCN, rt, 20 min		
	R^1			
	NH_2		(19) + N^2-isomer (20) + N^3-isomer (8)	271
	NO_2		(8) + N^2- + N^3-isomer (56)	
		NaH, MeCN, rt		271
	R^1			
	Cl	20 min	(36) + N^2-isomer (24)	
	Me	10 min	(45) + N^2-isomer (25)	
				
	R^1			
	Cl	NaOH (50%), THF, rt, 3 min	(42)	1358
	OMe	KOH, 18-crown-6, glyme, 20°, 10 min	(62) + N^2-β-isomer (31)	1292
	SMe	KOH, TDA-1, MeCN, rt, 15 min	(65) + N^1-α-isomer 95) + N^2-isomer (9)	1326

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

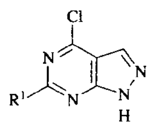
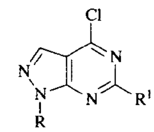
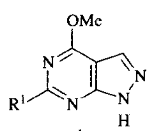
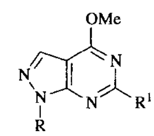
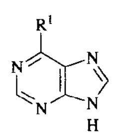
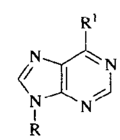
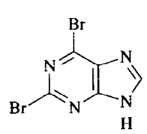
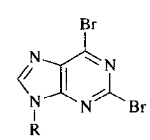
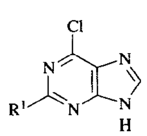
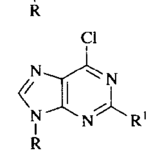
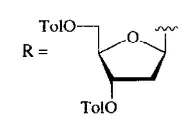
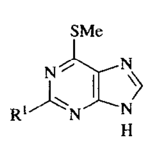
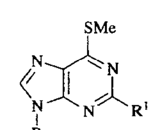
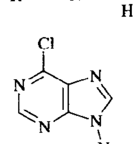
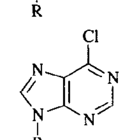
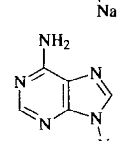
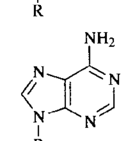
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
				
	R^1			
	Cl	NaOH (50%), CH_2Cl_2, Bu_4NHSO_4	(36)	1359
	NH_2	KOH, (30%), THF, CH_2Cl_2	(39) + N^2-isomer (39)	1360
				
	R^1			
	Cl	NaOH (50%), CH_2Cl_2, Bu_4NHSO_4	(48)	1359
	NH_2	KOH (30%), THF, CH_2Cl_2, rt, 2 min	(47) + N^2-isomer (13)	1360
	NH_2	KOH (50%), Bu_4NHSO_4, CH_2Cl_2, rt, 2 min	(37) + α-isomer (6) + N^2-β-isomer (15)	1360
	OMe	NaOH (50%), CH_2Cl_2, Bu_4NHSO_4	(40)	1359
		NaH, MeCN, rt, Me_2CO	 R^1: Cl, 30 min, (61) + N^7-isomer (13); Br, 1 h, (45) + N^7-β-isomer (13)	1297, 1361
		NaH, MeCN, rt, 15 min	 (50) + α-anomer (11)	1361, 1362
			 	
	R^1			
	Cl	NaH, MeCN, rt, 30 min	(59) + N^7-isomer (11)	1297
	NH_2	NaH, MeCN, rt, 30 min	(55) + N^7-isomer (9)	1297
	NHPh	NaH, MeCN, rt, 1 h	(43) + N^7-isomer (10)	1363
	NHC_6H_4Bu-*p*	NaH, MeCN, rt, 1 h	(64) + N^7-isomer (14)	1364
		NaH, MeCN, rt, 1 h		
			R^1 / — / N^7-β / N^9-α / N^7-α	
			SMe (62) (19) (0.3) (0.2)	1361, 1365
			Br (69) (15) (2) (0.8)	1361
		MeCN/THF (5:1), 10°, 10 h	 (18) + α-anomer (52)	1168
		Me_2CO, rt, 19 h	 (43)	65, 1366

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

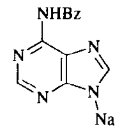
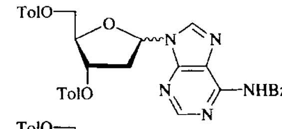
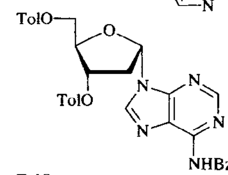
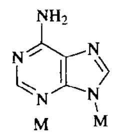
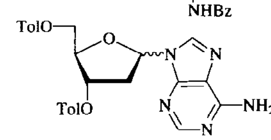
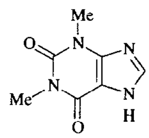
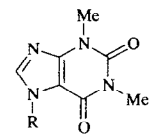
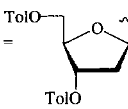
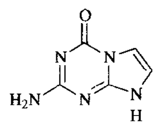
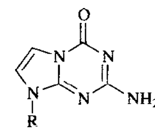
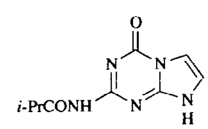
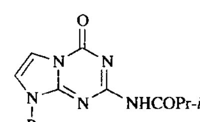
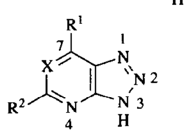
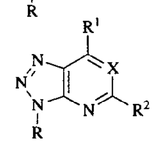
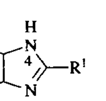
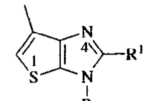
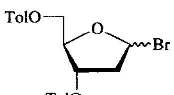
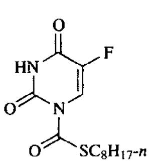
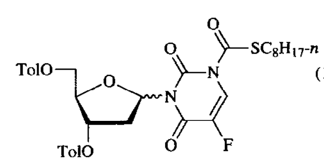
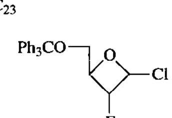
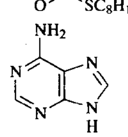
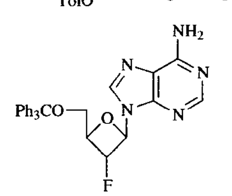
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		DME, rt, 24 h	 (46) α:β = 5:95	65
		MeCN, THF, 10°, 10 h	 (52) + β-anomer (18)	65
		MeCN, rt, 24 h		65
	M = K		(18) α:β = 57:43	
	M = Li		(17) α:β = 71:29	
		NaH, MeCN, rt, 10 min	 (74) R = 	1367
		K_2CO_3 (10%), CH_2Cl_2, Bu_4NHSO_4, rt	 (42) + α-anomer (21)	1368, 1369
		K_2CO_3, TDA-1, MeCN, rt, 1 h	 (29) + α-anomer (59)	1369
				
	X / R^1 / R^2		(N^3-α) (N^2-β) (N^2-α) (N^1-β) (N^4-α) (N^4-β)	
	CH / Cl / H	NaH, MeCN, rt, 30 min	(29) (11) (21) (5) (13) (—) (—)	1370
	N / NH_2 / H	K_2CO_3, TDA-1, DMF, rt, 20 min	(14) (13) (11) (12) (—) (4) (3)	270
	N / OMe / H	NaH, MeCN, rt, 30 min	(29) (—) (32) (—) (23) (—) (—)	270
	N / OMe / NH_2	KOH, TDA-1, MeCN, rt, 20 min	(20) (6) (19) (4) (13) (—) (—)	1371
	 R^1 = H, MeS, BnS	NaH, MeCN, rt, 1-2 h	 (63-88) + N^4-isomer (—)	350
 C_{23}		(i-Pr)$_2$NEt, THF, rt, 12 h	 (15)	256a
		K_2CO_3, 18-crown-6, DMF, 100°	 (40) + α-anomer (—)	1372

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TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

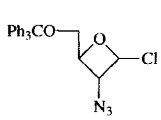
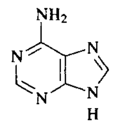
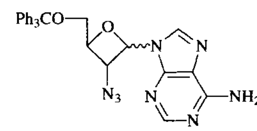
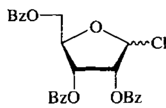
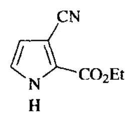
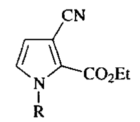
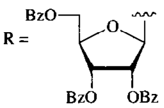
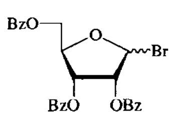
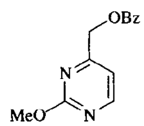
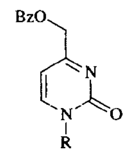
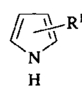
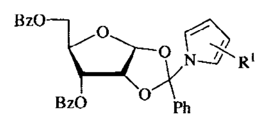
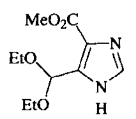
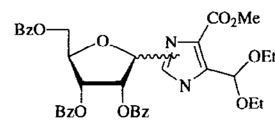
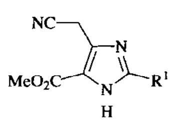
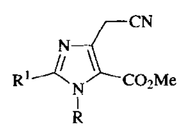
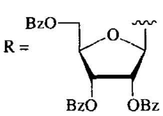
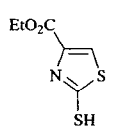
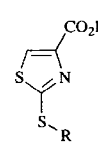
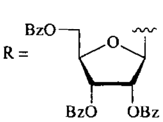
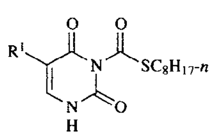
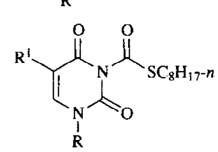
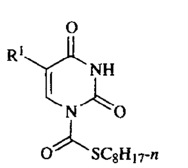
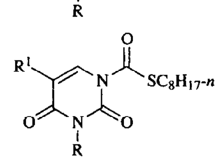
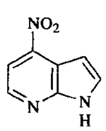
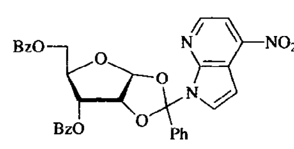
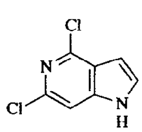
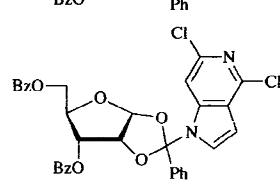
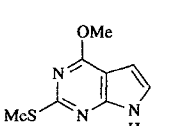
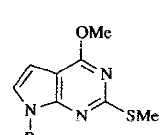
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		K_2CO_3, 18-crown-6, DMF, 100°	 (55) α:β = 1:2	1372
C_{26} 		NaH, MeCN, 70°, 17 h	 (96) R = 	1373, 1374
		Na_2CO_3, CH_2Cl_2, MeCN, rt, 24 h	 (63)	867
		NaH, dioxane, rt, 30 min, 50°, 1 h	 R^1: 2-CN (84); 3-CN (85)	68; 1297
		NaH, MeCN, 50°, 4 h	 (70) mixture of N^1 and N^3 isomers	1323
		NaH, MeCN, rt, 4 h	 R^1: Cl (69); SMe (72) R = 	1324
		NaH, MeCN, rt, 3 h	 (38) R = 	1375
		(*i*-Pr)$_2$NEt, DMF, rt, 12 h	 R^1: H (74); F (74)	1294
		(*i*-Pr)$_2$NEt, DMF, rt, 12 h	 R^1: H (78); F (79); Me (73)	1294
		NaH, MeCN, rt, 3 h	 (31)	1376
		NaH, MeCN, rt, 3 h	 (61)	1377
		NaOH (X%), CH_2Cl_2, Bu_4NHSO_4	 X: 10 (25), α-anomer (10); 50 (25), α-anomer (66)	1378; 1378

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

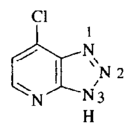
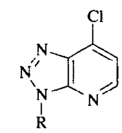
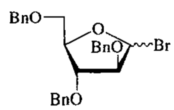
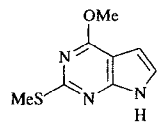
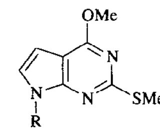
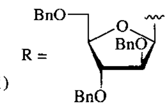
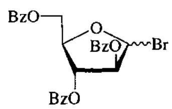
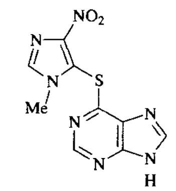
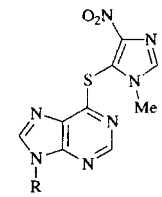
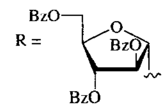
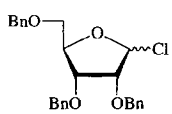
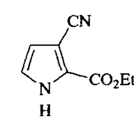
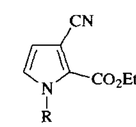
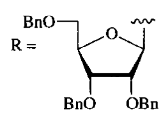
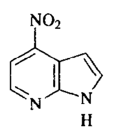
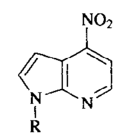
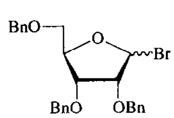
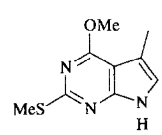
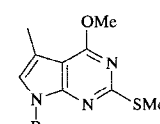
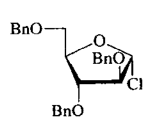
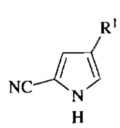
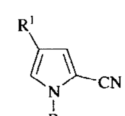
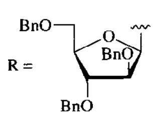
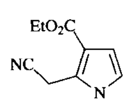
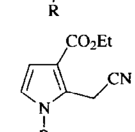
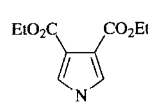
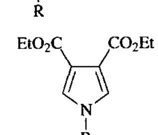
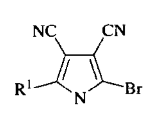
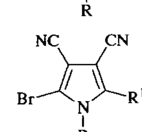
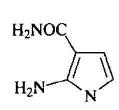
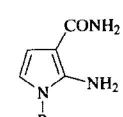
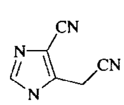
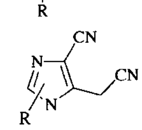
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		NaH, MeCN, rt, 24 h	 (30) + N^2-β-isomer (26) + N^1-β-isomer (21)	1370
		NaOH (50%), TEBA, CH_2Cl_2, rt, 15 min	 (63) + α-anomer (21) R = 	66
		NaH, MeCN, rt, 15 h	 (55) R = 	1092
		NaH, DMF, rt, 21 h	 (39) R = 	1373
		NaH, MeCN, rt, 6 h	 (42) + α-anomer (44)	1376
		NaOH (50%), TEBA, CH_2Cl_2, rt, 3 h	 (25) + α-anomer (45)	1379
		NaH, MeCN, rt, 12 h	 R^1: H (74); CN (87) R = 	68, 1315
		NaH, MeCN, rt, 2 h	 (82)	1317
		NaH, MeCN, rt	 (69)	1316
		1. $(CH_3)_2NCH(OEt)_2$ 2. NaH, MeCN, rt	 R^1: NH_2 30 min (—); N=CHOEt 12 h (79)	1297, 1316, 1380
		Et_3N, MeCN, 100°, 1.25 h	 (40)	352
		NaH, DMF, rt, 2 h	 (—)	354

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

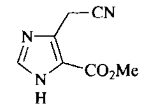
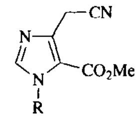
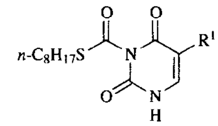
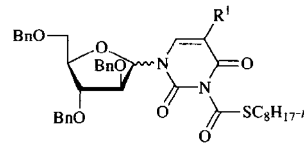
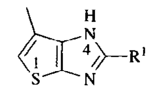
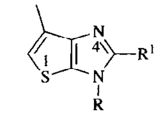
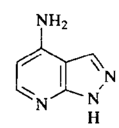
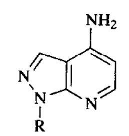
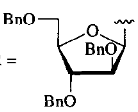
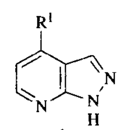
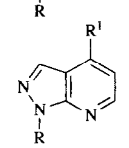
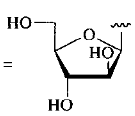
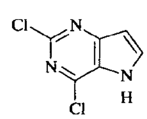
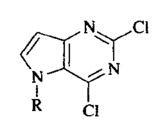
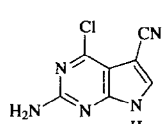
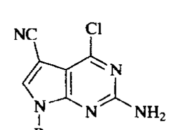
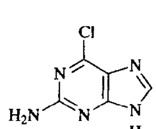
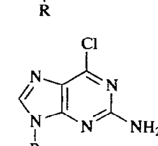
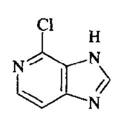
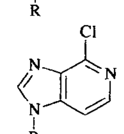
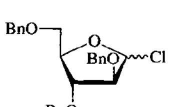
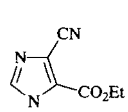
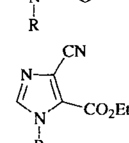
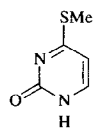
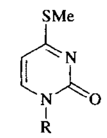
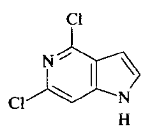
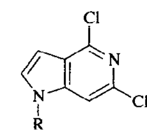
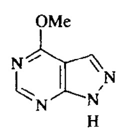
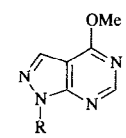
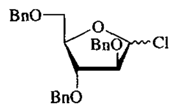
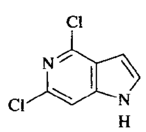
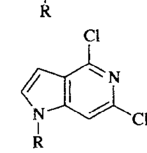
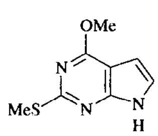
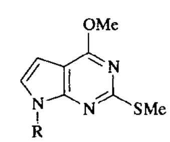
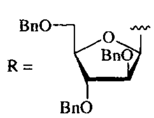
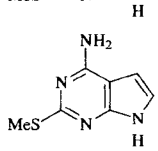
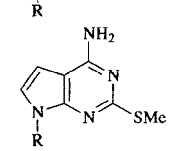
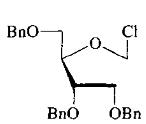
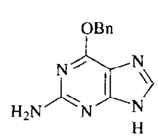
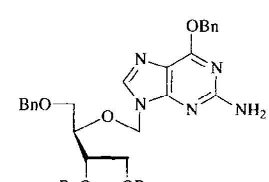
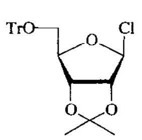
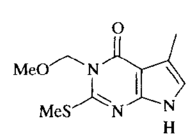
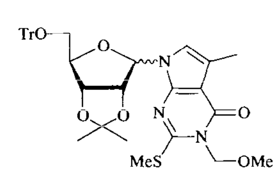
Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		NaH, DMF, rt, 2 h	 (—) + N^3-isomer; N^1:N^3 = 5:1.2	354
	 R¹: F, Me	*i*-Pr$_2$NEt, MeCN, rt, 12 h	 (99) α:β = 51:48; (84) α:β = 34:54	256a
	 R¹ = H, SMe, SBn	NaH, MeCN, rt, 48 h	 (50-60) + N^4-isomer (—)	350
		NaH, MeCN	 (—) R = 	1354
		1. NaH, MeCN, rt, 12 h	 R = 	
	R¹: H	2. Pd(OH)$_2$, cyclohexene, EtOH, reflux, 48 h	(60)	1303, 1354
	Cl	2. BCl$_3$, MeOH, rt, 30 min	(63)	1303, 1354
	OMe	2. Pd(OH)$_2$, cyclohexene, EtOH, reflux, 48 h	(44)	1303, 1354
	N$_3$	2. Pd(OH)$_2$, cyclohexene, EtOH, reflux, 48 h	(41)	1303, 1354
	OBn	2. Pd(OH)$_2$, cyclohexene, EtOH, reflux, 48 h	(64)	
		NaH, MeCN, rt, 6 h	 (81)	1353
		NaH, MeCN, rt, 12 h	 (58)	1299
		NaH, MeCN, rt, 15 h	 (68) + N^7-isomer (11)	1381
		NaH, DMF, rt, 2 h	 (—)	354
		NaH, DMF, rt, 27 h	 (59)	355

TABLE XI. REACTIONS OF ACIDIC HETEROCYCLES WITH 1-HALOSUGARS IN THE PRESENCE OF BASES (*Continued*)

Sugar	Base	Conditions	Product(s) and Yield(s) (%)	Refs.
		NaH, DMF, rt, 18 h	 (—)	356
		KOH, TDA-1, MeCN, 24°	 (78) + α-anomer (6)	349
		KOH, TDA-1, MeCN, rt, 50 min	 (43) + α-anomer (6) + N^7-isomer (25)	340
		KOH, TDA-1, MeCN	 (69)	1382
		NaOH (50%), Bu_4NHSO_4, C_6H_6, DME, 15 min	 (35) + α-anomer (57) R = 	348
		NaOH (50%), TEBA, CH_2Cl_2, rt, 15 min	 (69) + α-anomer (14)	1383
		NaH, DMF, rt, 18 h	 (33)	1165
C_{27} 		NaH, DMF, rt	 (81)	1384

12. Acknowledgments

We thank Schering AG and in particular Drs. U. Eder, B. Mueller, K. Specht, and G. Stock for their long-lasting and unfailing support of this review. We are furthermore obliged to Mr. W. Becker, Miss C. Heinz, Miss N. Schidniogrotski, and Mrs. M. Golde for patiently writing and rewriting the text and drawing all of the formulas for this review. H. Vorbrüggen also thanks his colleagues of the Department of Organic Chemistry, Free University of Berlin, for their kind hospitality since his retirement from Schering AG in 1995.

End Notes

This reaction is commonly cited in the literature as the Vorbrüggen Reaction (chapter editor).

*

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