$H_C/H_D$ locate the alanine sidechain and the C-terminal amide substituent essentially as shown in the stereopair diagram of the proposed complex. While $H_z$ shifts downfield (~0.5 ppm) as expected for hydrogen bond formation upon complexation, the control experiment using 1 could not be carried out due to 1's weak association with the alanine dipeptide.

Macrocycle 2 provides one of the few examples of an enantioselective host whose binding properties follow clearly from its structure. Knowing the detailed structure of the complex, we should now be able to improve enantioselectivity in a rational way. We will describe such studies in the near future.[5]

(5) This work was supported by Grant Number CHE89-11008 from the National Science Foundation.

# Mild Periodinane Oxidation of Protected Nucleosides To Give 2'- and 3'-Ketonucleosides. The First Isolation of a Purine 2'-Deoxy-3'-ketonucleoside Derivative[1,29]

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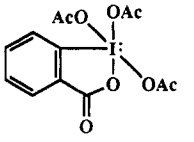
*Summary:* Oxidation of 3',5'- or 2',5'-bis-*O*-silyl-protected nucleosides with the Dess-Martin 12-I-5 periodinane reagent, 1,1,1-tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (I), in dichloromethane gives 2'- or 3'-ketonucleoside derivatives, respectively. Isolation of the first purine 2'-deoxy-3'-ketonucleoside derivative (**2d**) has been accomplished by periodinane oxidation of 5'-*O*-(*tert*-butyldiphenylsilyl)-2'-deoxyadenosine (**1d**).

Ketonucleoside derivatives are useful synthetic intermediates whose synthesis has attracted considerable attention.[2] The instability of pentofuranulosyl nucleosides, especially under basic conditions, was noted in the first attempted oxidation of 5'-*O*-tritylthymidine with $CrO_3$/pyridine which resulted in spontaneous $\beta$-elimination of thymine.[3] Loss of thymine also occurred during the mild Pfitzner-Moffatt (DMSO/DCC) oxidation of 5'-*O*-acetylthymidine.[4] Moffatt and co-workers oxidized 3',5'- and 2',5'-di-*O*-trityluridine[5] and cytidine[6] derivatives with DMSO/DCC to obtain the first reported furanosyl 2'- and 3'-ketonucleosides. Rosenthal et al. oxidized 9-(3,5-*O*-isopropylidene-$\beta$-D-xylofuranosyl)adenine with $RuO_4$ to give a protected purine 2'-ketonucleoside.[7] Antonakis and co-workers prepared theophylline hexopyranosyl 2'- and 4'-ketonucleosides with Cr(VI) and DMSO/DCC oxidants.[8] Sasaki et al. have obtained furanosylpyrimidine 2'-ketonucleosides from elimination reactions,[9] and the [1,2]-hydride shift rearrangement[10] of 3'-*O*-tosyl-5'-*O*-trityluridine to a 2'-keto-3'-deoxyribonucleoside with a Grignard reagent[10a] has been described.[11]

Binkley et al. irradiated the 3'-pyruvate ester of 5'-*O*-tritylthymidine to obtain the first pyrimidine 2'-deoxy-3'-ketofuranosyl nucleoside.[12] Garegg and co-workers[13] reported smooth oxidation of partially protected carbohydrates with $CrO_3$/pyridine/$Ac_2O$, and we applied that reagent for the efficient synthesis of 3'- or 2'-ketonucleoside derivatives from 2',5'- or 3',5'-diprotected nucleosides and 5'-protected 2'- or 3'-deoxynucleosides.[14] Crews and Baker[15] prepared 2'- and 3'-ketoadenosines by Pfitzner-Moffatt oxidation, and deprotection of adenosine derivatives. Bergstrom and co-workers[16] recently noted an improved yield (80%) of 3'-keto-5'-*O*-tritylthymidine by oxidation of 5'-*O*-tritylthymidine with pyridinium dichromate/molecular sieves.[8] The Swern modification (DMSO/oxalyl chloride)[17] of the Moffatt oxidation was applied to nucleosides by Ueda et al.[18] We investigated that procedure but found significant contamination by heterocyclic *N*- and *O*-(methylthio)methyl derivatives with Swern oxidation[17] of lactam-containing nucleosides (e.g. uridine and inosine).

The Dess-Martin[19] 12-I-5 periodinane reagent, 1,1,1-tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (I) (*CAUTION*[29]), effected smooth and efficient oxidation of a silyl-protected adenosine derivative.[20] This method is general and convenient for oxidations of 3',5'- and 2',5'-bis-*O*-silyl-protected nucleosides to 2'- and 3'-ketonucleoside derivatives. These mild conditions allow preparation and isolation of a purine 2'-deoxy-3'-ketonucleoside for the first time.




I

Oxidation of 2',5'-bis-*O*-TBDMS-uridine[21] (**1a**) by the general procedure[22] afforded crystalline 2',5'-bis-*O*-

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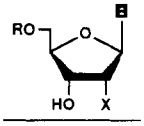
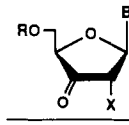
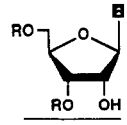
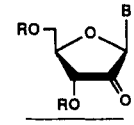
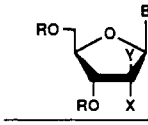
**Table I. Structures of Starting and Product Nucleosides**[a]

| | | | | |
|---|---|---|---|---|
|  |  |  |  |  |
| B R X | B R X | B R | B R | B R X Y |
| 1a U Si OSi | 2a U Si OSi | 3a U Si | 4a U Si | 5 A Si OH OH |
| 1b A Si OSi | 2b A Si OSi | 3b A Si | 4b A Si | 6 A H H OH |
| 1c T Tr H | 2c T Tr H | 3c C $Si_2$ | 4c C $Si_2$ | 7 C H H OH |
| 1d A Si′ H | 2d A Si′ H | 3d G $Si_2$ | 4d G $Si_2$ | 8 G $Si_2$ OH OH |
| 1e A H H | | 3e A H | | 9 G $Si_2$ H OH |
| | | 3f C H | | 10 G H H OH |
| | | 3g G H | | |

[a] Abbreviations: U = uracil-1-yl; A = adenin-9-yl; T = thymin-1-yl; C = cytosin-1-yl; G = guanin-9-yl; Si = TBDMS (*tert*-butyldimethylsilyl); Si′ = TBDPS (*tert*-butyldiphenylsilyl); $Si_2$ = TPDS (1,1,3,3-tetraisopropyldisiloxan-1,3-diyl); Tr = triphenylmethyl.

TBDMS-3′-ketouridine[14b] (**2a**, 97%), and 3′,5′-bis-*O*-TBDMS-uridine[21] (**3a**) gave crystalline 3′,5′-bis-*O*-TBDMS-2′-ketouridine[14b] (**4a**, 95%). Treatment of 2′,5′-bis-*O*-TBDMS-adenosine[21] (**1b**) with 4 equiv of I gave the 3′-ketonucleoside[14b] (**2b**, 96%) as a slightly yellow powder, whose high purity was indicated by its reduction and deprotection to give 9-(β-D-xylofuranosyl)adenine in 94% overall yield.[20]

Treatment of 0.25 g (0.5 mmol) of 3′,5′-bis-*O*-TBDMS-adenosine[21] (**3b**) with I (2.3 equiv) gave 0.27 g of an orange glass that contained ~80% of (**4b** + **5**) by UV analysis. The $^1H$ NMR ($Me_2SO$-$d_6$) spectrum of this mixture indicated **4b**[14b] and its hydrate (**5**) in a ratio of ~3:1. Its $^{13}C$ NMR spectrum had signals at δ 208.35 (C2′ carbonyl of **4b**) and 98.43 (C2′ *gem*-diol of **5**). A closely corresponding signal at δ 98.9 was reported by Rapoport and co-workers for the *gem*-diol carbon of a 5-membered cyclic ketone hydrate of saxitoxin,[23] and hydration of 2′-ketoadenosine analogues has been documented.[7,15] This mixture was treated with sodium triacetoxyborohydride and deprotected as described[20] to give 9-β-D-(arabinofuranosyl)-adenine (**6**) and adenosine (**3e**) (97:3) in 70% overall yield from **3b**.

Oxidation of 0.15 g (0.30 mmol) of 3′,5′-*O*-TPDS-cytidine[24] (**3c**) required 3.5 equiv of I to give a yellow glass (0.16 g, containing ~75% of **4c** by UV) whose $^1H$ NMR spectrum ($Me_2SO$-$d_6$) had peaks corresponding to those reported for 3′,5′-*O*-TPDS-2′-ketocytidine[14b] (**4c**). Subjection of this material to the reduction–deprotection sequence[20] afforded 1-(β-D-arabinofuranosyl)cytosine (**7**) plus cytidine (**3f**) (9:1, 60% overall from **3c**). Treatment of 0.11 g (0.20 mmol) of 3′,5′-*O*-TPDS-guanosine[24] (**3d**) with 2.3 equiv of I gave 0.12 g of a yellow glass [containing ~75% of (**4d** + **8**) by UV] whose $^1H$ NMR spectrum ($Me_2SO$-$d_6$) indicated the 2′-ketoguanosine derivative (**4d**) plus its hydrate (**8**) ~1:4). Reduction of this material with sodium triacetoxyborohydride afforded 9-(3,5-*O*-TPDS-β-D-arabinofuranosyl)guanine[25] (**9**) plus **3d** (80% combined). After deprotection, HPLC analysis indicated 9-(β-D-arabinofuranosyl)guanine[14b] (**10**) and guanosine (**3g**) in a ratio of ~3:1.

Treatment of 1 mmol of 5′-*O*-tritylthymidine[26] (**1c**) with 1.5 equiv of I afforded a colorless glass that was crystallized from $CH_2Cl_2$/hexane to afford 3′-keto-5′-*O*-tritylthymidine (**2c**) in 93% yield with melting point and $^1H$ NMR spectral data identical with those described.[12] This represents the highest yield reported[12,14,16] for the synthesis of this sensitive compound (**2c**).

Treatment of 2′-deoxyadenosine (**1e**) with *tert*-butyldiphenylsilyl chloride (1.5 equiv) in pyridine gave 5′-*O*-TBDPS-2′-deoxyadenosine[27] (**1d**, 91%). Oxidation[22] of 1 mmol of **1d** with 2 equiv of I gave 5′-*O*-TBDPS-2′-deoxy-3′-ketoadenosine[28] (**2d**) quantitatively. This **2d** has not undergone detected ($^1H$ NMR) decomposition at 0 °C for several months and is the first example of a "stable" purine 2′-deoxy-3′-ketonucleoside. A small sample of **2d** was stable at ~40 °C for several hours, but decomposed slowly upon heating at ~55 °C and rapidly upon exposure to $Me_2SO$-$d_6$.

**Conclusions.** The Dess–Martin 12-I-5 periodinane reagent[19] (I) effects smooth and efficient oxidation of 3′,5′- and 2′,5′-bis-*O*-silyl nucleosides to their 2′- and 3′-keto derivatives. This affords a valuable new alternative to Moffatt/Swern-type reagents, that give (methylthio)-

(22) A solution of 2′,5′-bis-*O*-TBDMS-uridine (**1a**, 0.47 g, 1 mmol) in $CH_2Cl_2$ (3 mL) was added to I[19] (0.64 g, 1.5 mmol) in $CH_2Cl_2$ (7 mL) at 0 °C. Stirring was continued at 0 °C for 15 min followed by warming to ambient temperature (*CAUTION*[29]). Reaction progress was monitored by TLC. After ~4 h the mixture was diluted with $Et_2O$ (30 mL), poured into 20 mL of ice-cold saturated $NaHCO_3/H_2O$ containing $Na_2S_2O_3 \cdot 5H_2O$ (2.5 g, 10 mmol), and shaken for 5 min. The organic phase was separated and washed with saturated $NaHCO_3/H_2O$, $H_2O$, and saturated NaCl/$H_2O$, dried ($Na_2SO_4$), and concentrated in vacuo at ambient temperature to give a colorless solid foam. Its crystallization from EtOAc/hexane afforded **2a** (0.45 g, 97%) as colorless microcrystals with mp 172–173 °C (lit.[14b] mp 177 °C); $^1H$ NMR spectrum identical with that reported.[14b]

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(25) Homogeneous **9**, obtained by flash chromatography, comigrated (HPLC) with a sample prepared by treatment of 9-(β-D-arabinofuranosyl)guanine with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane.[24]

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(27) Compound **1d**: mp 129–130 °C; $^1H$ NMR ($CDCl_3$,$Me_4Si$) δ 1.10 (s, 9, Si-*t*-Bu), 2.50 (ddd, *J* = 13.5, 6.2, 4.2 Hz, 1, H2′), 2.56 (br s, 1, OH3′), 2.74 (dt, *J* = 13.5, 6.5 Hz, 1, H2″), 3.82 (dd, *J* = 11.0, 4.1 Hz, 1, H5′), 3.90 (dd, *J* = 11.0, 4.5 Hz, 1, H5″), 4.06 ("q", *J* = 4 Hz, 1, H4′), 4.71 (m, 1, H3′), 5.63 (br s, 2, $NH_2$), 6.43 ("t", *J* = 6.5 Hz, 1, H1′), 7.30–7.70 (m, 10, $SiPh_2$), 8.00 (s, 1, H2), 8.29 (s, 1, H8); MS *m*/*z* 489 (2, $M^+$), 432 (100, M − *t*-Bu).

(28) Compound **2d** was a powder with mp 85 (softening)–95 °C (liquid): UV (MeOH) max 260 nm (ε 14300); $^1H$ NMR ($CDCl_3$, $Me_4Si$) δ 1.00 (s, 9, Si-*t*-Bu), 3.18 (d, *J* = 7.2 H, 2, H2′,2″), 4.00 ("d", *J* = 2.8 Hz, 2, H5′,5″), 4.24 ("t", *J* = 2.8 Hz, 1, H4′), 5.80 (br s, 2, $NH_2$), 6.58 (t, *J* = 7.2 Hz, 1, H1′), 7.20–7.70 (m, 10, $SiPh_2$), 8.08 (s, 1, H2), 8.26 (s, 1, H8); $^{13}C$ NMR ($CDCl_3$, $Me_4Si$) δ 43.02 (C2′), 63.80 (C5′), 81.16 (C1′), 83.43 (C4′), 120.10 (C5), 138.90 (C8), 150.05 (C4), 153.66 (C2), 156.08 (C6), 209.71 (C3′); MS *m*/*z* 352 (2, M − BH), 295 (100, M − B − *t*-Bu). Anal. Calcd for $C_{26}H_{29}N_5O_3Si$: C, 64.04; H, 5.99; N, 14.36. Found: C, 63.82; H, 6.01; N, 14.18.

(29) **Note added in proof**: J. B. Plumb and D. J. Harper (*Chem. Eng. News* July 16, 1990, page 3) have reported the explosion of 2-iodoxybenzoic acid upon impact with a steel hammer or ball, or upon heating to 154 °C. They also noted violent decomposition of the Dess–Martin reagent (I) at 130 °C, but not upon impact. Our general procedure[22] employs a range of 0 °C to ambient temperature, and we have observed no abrupt decomposition of the reagent (I) or precursors during a large number of experiments by two persons. However, large-scale reactions or oxidations at elevated temperatures should be approached with appropriate caution when using hypervalent iodine compounds.

methyl byproducts or toxic chromium(VI) oxidants for the preparation of ketonucleosides. Easy isolation of the 2-iodobenzoic acid byproducts and their reconversion to the periodinane reagent[19] (I) make this an economically feasible oxidant. Oxidation of 5′-*O*-tritylthymidine (**1c**) with I has provided the corresponding 2′-deoxy-3′-ketonucleoside (**2c**) in the highest yield (93%) presently reported. Preparation and characterization of 5′-*O*-TBDPS-2′-deoxy-3′-ketoadenosine (**2d**), the first "stable" purine 2′-deoxy-3′-ketonucleoside derivative, has been achieved by oxidation of 5′-*O*-TBDPS-2′-deoxyadenosine (**1d**) with I.

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# A Concise Approach to β-(1→6)- and β,β-(1→1)-Linked *C*-Disaccharides. The Synthesis of *C*-β,β-Trehalose Peracetate

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*Summary:* The fluoride ion mediated condensation of the tetraacetate of β-*C*-glucopyranosylnitromethane with *aldehydo* sugars, followed by the elaboration of the resulting nitroaldol, provides an expeditious approach to β-(1→6)-linked (from hexodialdose derivatives) and β,β-(1→1)-linked (from *aldehydo*-hexoses) *C*-disaccharides. *C*-β,β-Trehalose peracetate, **13**, the first example of a *C*-disaccharide related to the trehaloses, was prepared using this methodology.

The replacement of the interglycosidic oxygen atom in disaccharides by a methylene group generates a class of extremely interesting, nonmetabolizable analogues of disaccharides, namely *C*-disaccharides. As chemically inert isosters of natural disaccharides, these pseudodisaccharides constitute potential inhibitors of glycosidases[1] and disaccharidases such as those present in the digestive tract.[2] The interest of these compounds is further supported by the recent discovery of the antiretroviral activity of certain glycosidase inhibitors (e.g., castanospermine).[3]

Since the first synthesis of a *C*-disaccharide by Sinaÿ and Rouzaud[4] (D-Glc-*C*-β-(1→6)-D-GlcOMe), several approaches to *C*-disaccharides have been investigated,[5,6] and the syntheses of such analogues as *C*-maltose,[5a] *C*-cellobiose,[5a] and others[5b-f] have been reported. Because of the difficulties inherent to the coupling of two sugar units by way of a carbon–carbon linkage, the first successful syntheses of *C*-disaccharides represent a major achievement. The long synthetic sequences involved limit, however, the availability of the final product. Our interest in *C*-disaccharides and derivatives as potential therapeutic agents for metabolic diseases prompted us to develop novel and short approaches to this type of pseudodisaccharides. We report, in this paper, a concise methodology for the synthesis of β-(1→6)- and β,β-(1→1)-linked *C*-disaccharides and its application to the preparation of two novel *C*-disaccharides, namely D-Glc-*C*-β-(1→6)-D-Gal (**7**) and *C*-β,β-trehalose peracetate (**13**).

Our approach is based on the utilization of *C*-glycosylnitromethane derivatives (e.g., **1**), available in two steps from the parent hexose,[7] as C-nucleophilic reaction partners. As suggested by the successful condensation of a 5-deoxy-5-*C*-nitroribofuranose derivative with *aldehydo* sugars,[8] and by the successful silylation of **1** to the corresponding silyl nitronates,[9] it was expected that the nitronate anion derived from **1** would be stable and could be used as a C-nucleophile *without concurrent β-elimination.* Indeed, the fluoride ion mediated[8,10] nitroaldol condensation of **1** with D-galactose-derived aldehyde **2** afforded the 7-deoxy-7-nitrotridecose derivative **3** in 52% yield[11] as one major diastereomer. The auxiliary functional groups of **3** were then removed in three steps (Scheme I): (1) acetylation–elimination of acetic acid, to give nitroalkene **4** [90%; *E*/*Z* mixture (~1:1), slowly isomerizing to *Z* only; *Z* isomer, δ H-6, 6.305; *E* isomer, δ H-6, 7.30]; (2) selective reduction of the double bond of **4** using $NaBH_4$,[12] to give 7-nitro derivative **5** (59%; ratio of epimers at C-7, 8:1); (3)

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