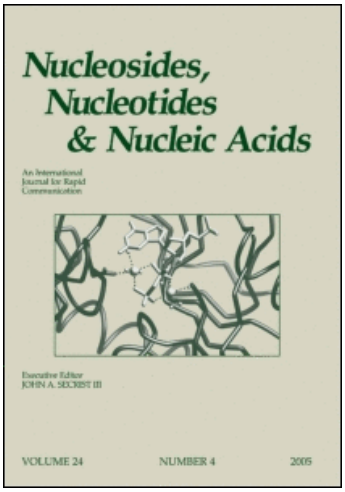


Nucleosides, Nucleotides and Nucleic Acids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597286

Nucleosides/Tides Abstracts

Marshall W. Logue[a]
[a] Michigan Technological University,

To cite this Article Logue, Marshall W.(1985) 'Nucleosides/Tides Abstracts', Nucleosides, Nucleotides and Nucleic Acids, 4: 4, 539 — 543
To link to this Article: DOI: 10.1080/07328318508081299
URL: http://dx.doi.org/10.1080/07328318508081299

NUCLEOSIDES & NUCLEOTIDES, 4(4), 539-543 (1985)

NUCLEOSIDES/TIDES ABSTRACTS

Compiled by Dr. Marshall W. Logue, Michigan Technological University

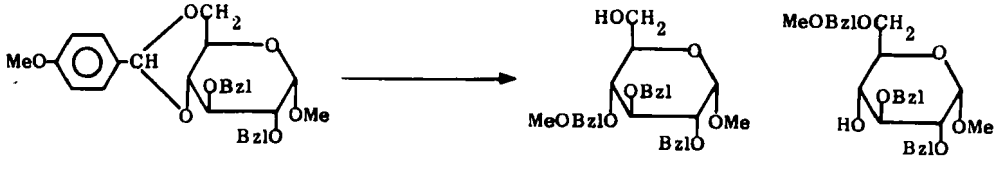
Glycosyl Isothiocyanates: A New Synthetic Procedure

$$\text{gly-X} + \text{KSCN} \xrightarrow[CH_3CN]{Bu_4N^+X^-} \text{gly-N=C=S}$$

Glycosyl halides react with suspensions of potassium thiocyanate in acetonitrile in the presence of molecular sieves and tetrabutylammonium salts (HSO_4, Br, I) to give glycosyl isothiocyanates in moderate to good yield. Isolated yields of 55-75% (70-90% based upon glycosyl halide used up) were realized with derivatives of glucopyranosyl, ribofuranosyl, arabinopyranosyl, and mannopyranosyl halides. Sugars with 2-O-acyl functions give, as expected, only isothiocyanates with 1,2-trans configurations. Glycosyl thiocyanates appear to be produced initially, which then isomerize to the isothiocyanates [Complete Experimental].

M. J. Camarasa, P. Fernandez-Resa, M. T. Garcia-Lopez, F. G. de las Heras, P. Mendez-Castrillon, and A. S. Felix, Synthesis, 509-510 (1984).

Regioselective Reductive Cleavage of 4-Methoxybenzylidene Acetals



Bzl = $C_6H_5CH_2$

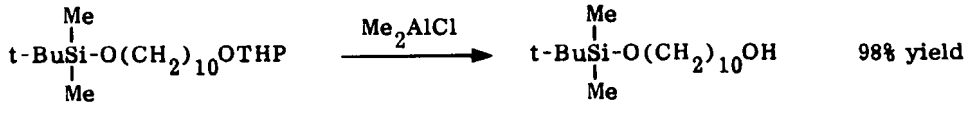
$NaBH_3CN/CF_3CO_2H/$ DMF — 9% — 85%

$NaBH_3CN/Me_3SiCl/CH_3CN$ — 76% — 13%

4-Methoxybenzylidene acetals can be regioselectively cleaved in a reductive manner to give mono-4-methoxybenzyl-protected diols. The 4,6-O-(4-methoxybenzylidene) derivatives of gluco- and mannopyranosides undergo ring opening to give the corresponding 4-O-(4-methoxybenzyl) derivatives in 76 and 83% yields, respectively, upon treatment with sodium cyanoborohydride in the presence of trifluoroacetic acid in DMF, whereas they ring open to give the 6-O-(4-methoxybenzyl) derivatives (85 and 89% yields, respectively) with sodium cyanoborohydride and trimethylsilyl chloride in acetonitrile. The 4-methoxybenzyl group can be selectively removed, in high yield (95-98%), in the presence of other benzyl ethers by treatment with cerium (IV) ammonium nitrate in aqueous acetonitrile [Partial Experimental].

R. Johansson and B. Samuelsson, J. Chem. Soc., Chem. Commun., 201-202 (1984).

Selective Cleavage of Tetrahydropyranyl Ethers in the Presence of t-Butyldimethylsilyl Ethers

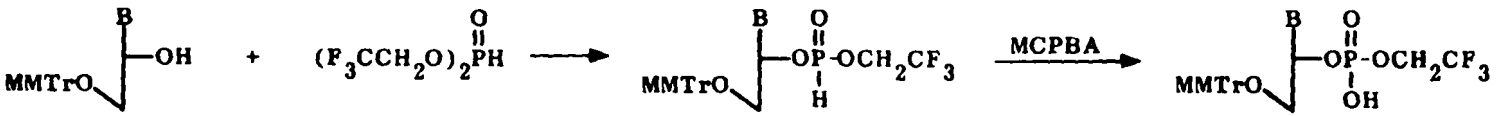


Tetrahydropyranyl ethers can be cleaved nearly quantitatively without any cleavage of t-butyldimethylsilyl ethers when treated with dimethylaluminum chloride (2 equivalents) in dichloromethane at -25 °C - r.t. for 1 h followed by an aqueous bicarbonate work-up. Three rather more complex examples are given that contain fairly sensitive functionalities (e.g., β-lactams) and are selectively deprotected in 89-100% yields. Methoxymethyl (MOM) and methoxyethoxymethyl (MEM) ethers are converted into the corresponding ethyl ethers by dimethylaluminum chloride, whereas 1-ethoxyethyl ethers are partially cleaved and partially converted into isopropyl ethers [Partial Experimental].

T. Ogawa and M. Shibasaki, Tetrahedron Lett., **25**, 663-664 (1984).

Di(2,2,2-Trifluoroethyl) Phosphonate: Phosphorylation Without Coupling Agents

5'-O-Protected deoxyribonucleosides are phosphorylated in good yield (87-92%) when treated with di(2,2,2-trifluoroethyl) phosphonate at 50 °C in the absence of coupling agents followed by oxidation of the resulting 3'-O-phosphonate with m-chloroperbenzoic acid. The phosphorylating agent is readily prepared by successive treatment of phosphorous trichloride with one equivalent of t-butyl alcohol and two equivalents of 2,2,2-trifluoroethanol in

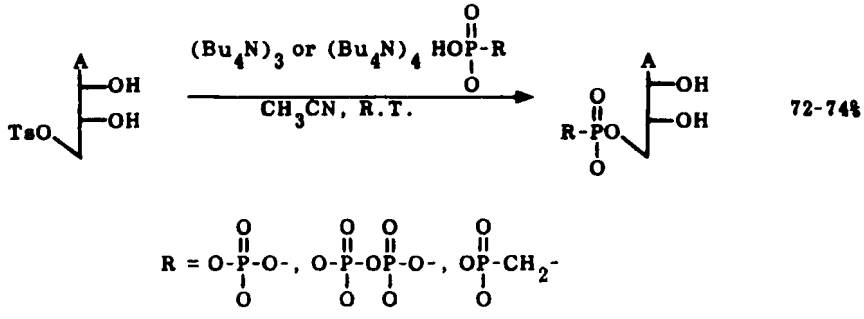


B = T, d-bzA, d-bzC, d-ibuG

dichloromethane at 0-5 °C. The trinucleotide d-GpApT was prepared via the phosphotriester method using this phosphorylating agent in 43% overall yield. Removal of the 2,2,2-trifluoroethyl blocking group is accomplished by treatment with tetramethylguanidinium p-nitrobenzaldoximate in dioxane-water (2:1 v/v) for 24 h at room temperature [Partial Experimental].

H. Takaku, H. Tsuchiya, K. Imai, and D. R. Gibbs, Chemistry Lett., 1267-1270 (1984).

Phosphorylation of Adenosine by Nucleophilic Displacement on the 5'-Tosylate



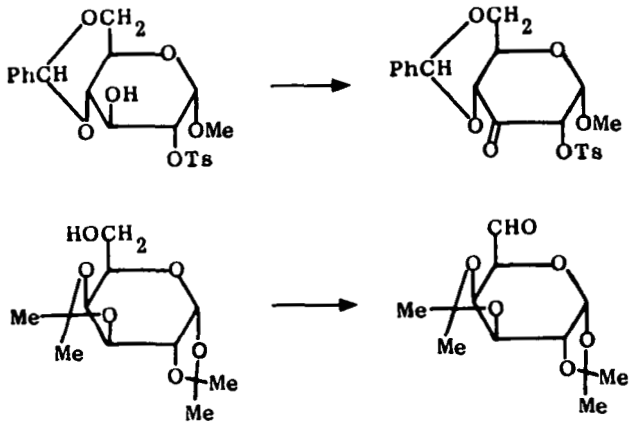
Adenosine 5'-diphosphate, 5'-triphosphate, and 5'-methylenediphosphonate are easily synthesized, in good yield, by nucleophilic displacement on adenosine 5'-tosylate with tetrabutylammonium monohydrogen salts of diphosphate, triphosphate, and methylenediphosphonate in acetonitrile, respectively. A significantly shorter reaction time (9 vs. 48 h) and a higher yield (93 vs. 74%) resulted when nucleophilic displacement by diphosphate was conducted with the 2',3'-O-isopropylidene derivative of the tosylate instead of with the 5'-tosylate itself.

This new phosphorylation method should be very amenable to the synthesis of phosphate analogs, such as the 5'-methylenediphosphonate above, which would be more difficult to prepare by the standard phosphorylation methods [Partial Experimental].

V. M. Dixit and C. D. Poulter, Tetrahedron Lett., **25**, 4055-4058 (1984).

Pyridinium Dichromate–Acetic Anhydride: New Oxidant for Sugars

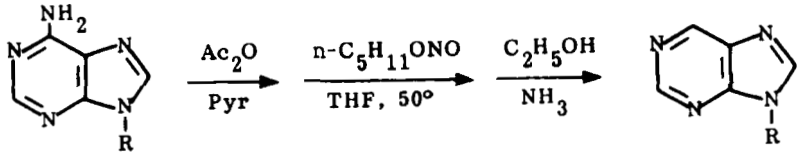
Secondary hydroxyls of sugars and nucleosides are readily and efficiently oxidized to ketones in dichloromethanes by 0.6 molar equivalents of pyridinium dichromate in the presence of 3.0 molar equivalents of acetic anhydride. Primary hydroxyls are oxidized to aldehydes with 0.7 and 3.0 molar equivalents



of pyridinium dichromate and acetic anhydride, respectively. DMF inhibits the further oxidation of aldehydes to carboxylic acids. Thus a 4:1 mixture of CH_2Cl_2:DMF is used as the solvent. Carboxylic acids are readily produced when increased amounts of oxidant are used. Benzylidene acetals are stable to this oxidant even after 16 h at reflux. The highly unreactive hydroxyl of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose is readily oxidized (96% yield). The nucleoside 3',5'-O-tetraisopropyldisiloxanyluridine is oxidized to the corresponding 2'-keto derivative in 89% yield [Partial Experimental].

F. Anderson and B. Samuelsson, Carbohydr. Res., **129**, C1-C3 (1984).

Reductive Deamination of 6-Aminopurine Nucleosides



R = ribofuranosyl, 2-deoxyribofuranosyl, arabinofuranosyl

Acetylated 6-aminopurine nucleosides are reductively deaminated upon heating (50 °C optimum) with n-pentyl nitrite in anhydrous THF under nitrogen. Yields range from 46 to 81%. Hydrogen donors other than THF were inferior. 2-Deazaadenosine and 8-azaadenosine are also deaminated in 46 and 81% yields, respectively. The carbohydrate hydroxyls must be protected to prevent transesterification and to increase the nucleosides solubilities [Complete Experimental].

V. Nair and S. D. Chamberlain, Synthesis, 401-403 (1984).
