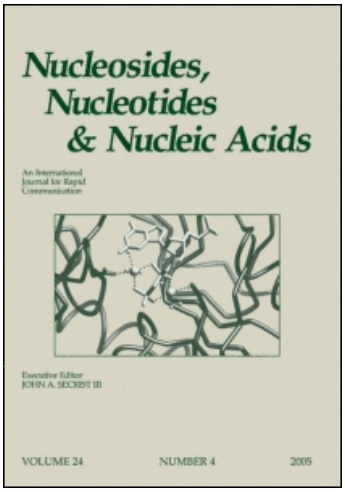

Nucleosides, Nucleotides and Nucleic Acids
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Nucleosidesfi/Ides Abstracts

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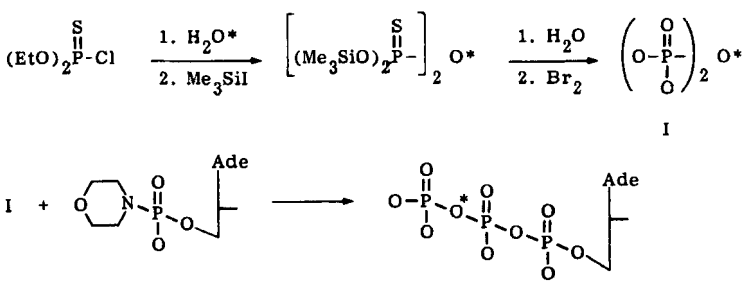
NUCLEOSIDES & NUCLEOTIDES, 3(3), 319-323 (1984)

NUCLEOSIDES/TIDES ABSTRACTS

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

Synthesis for Bridge-Oxygen Labeled Nucleoside Triphosphates

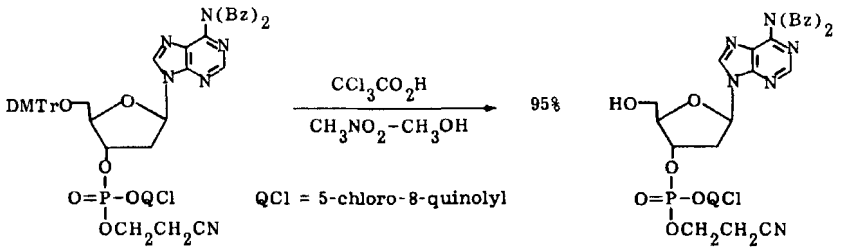


Adenosine 5'-[β,γ-^{18}O] triphosphate has been synthesized with 97% oxygen-18 incorporation via coupling of bridge-oxygen labeled pyrophosphate and adenosine 5'-phosphomorpholidate in 72% yield. The bridge-labeled pyrophosphate itself was synthesized via a four-step procedure from diethyl thiophosphorochloridate in 54% overall yield (based on $H_2{}^{18}O$). Because the nucleotide is coupled to the pyrophosphate in the last step, this method can be readily used to prepare other bridge-labeled nucleoside triphosphates [partial experimental].

P. M. Cullis, J. Am. Chem. Soc., **105**, 7783-7784 (1983).

0732-8311/84/0303-0319$3.50/0

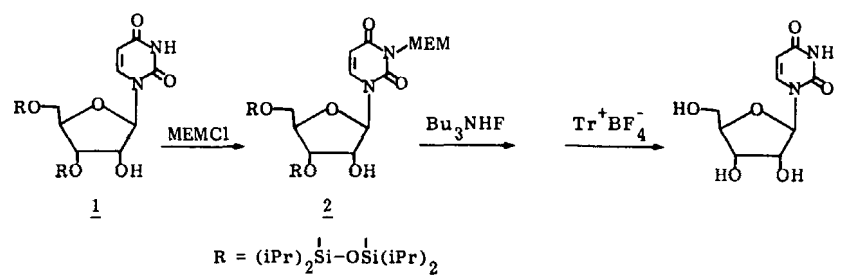
Selective Removal of 5'-O-Dimethoxytrityl Groups with Trichloroacetic Acid



A 3% solution of trichloroacetic acid in nitromethane-methanol (95:5) will cleave the 5'-O-dimethoxytrityl group from protected 2'-deoxyadenosines within 5 min without any detectable depurination. This reagent also effectively cleaves the dimethoxytrityl group from 2'-deoxyadenosine-3'-phosphates and 2'-deoxyadenosine-containing oligonucleotides without any detectable depurination. Although $ZnBr_2$-CH_3NO_2 (a reagent developed to minimize depurination) exhibits depurination rates comparable to those for 3% trichloro acetic acid, its detritylation rates are much slower than those for the latter [partial experimental].

H. Takaku, K. Morita, and T. Sumiuchi, Chemistry Lett., 1661-1664 (1983).

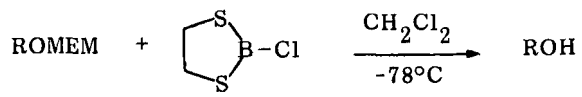
Methoxyethoxymethyl Group: Protection of Uracil Ring During Oligoribonucleotide Synthesis



The methoxyethoxymethyl group (MEM) can be selectively introduced into the uracil moiety of 3',5'-protected uridines. The MEM group is stable to conditions used to remove other protecting groups commonly used in oligoribonucleotide synthesis; e.g., 80% HOAc, triethylamine, and the tetramethylguanidinium salt of 2-pyridine carboaldoxime, but is readily removed in 1 h by treatment at room temperature with trityl fluoroborate. MEM protected uridine **2** is available in 71% yield from **1**. Also, UpUpA is synthesized from **2** in approximately 30% overall yield [partial experimental].

H. Takaku, S. Ueda, and T. Ito, Tetrahedron Lett., **24**, 5363-5366 (1983).

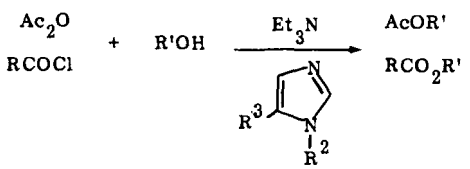
Selective Removal of Methoxyethoxymethyl (MEM) Ethers



MEM ethers can be selectively cleaved by 2-chloro-1,3,2-dithioboralan (**1**) at -78°C in the presence of allyl, benzyl, methyl, tert-butyldimethylsilyl, and tert-butyldiphenylsilyl ethers, esters, methylene acetals, and some tetrahydropyranyl ethers. However, methoxymethyl ethers and isopropylidene and benzylidene acetals cleave at rates comparable to MEM ethers. Primary MEM ethers can be selectively cleaved in the presence of secondary MEM ethers. The deprotected alcohols are generally produced in >80% yield [partial experimental].

D. R. Williams and S. Sakdarat, Tetrahedron Lett., **24**, 3965-3968 (1983).

1-Alkylimidazoles: Efficient Catalysts for Acylation of Alcohols



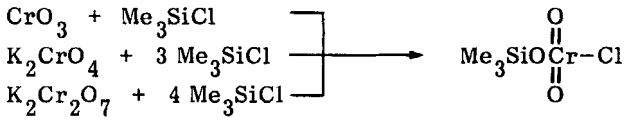
1, R^2 = iPr, R^3 = H
2, R^2 = iPr, R^3 = Me
3, R^2 = 4-MeOPhCH$_2$, R^3 = Me

1-Alkylimidazoles accelerate the acylation of alcohols with acid anhydrides or acid chlorides. A series (22) of 1-alkylated, 1,2-dialkylated, 1,4-dialkylated, and 1,5-dialkylated imidazoles have been prepared, and their catalytic activity compared to that of 4-dimethylaminopyridine (DMAP). In the acetylation of 4-methyl-2-pentanol with acetic anhydride, **2** and **3** are more effective than DMAP. However, they are less effective than DMAP in the acetylation of the sterically hindered tert-butyl alcohol.

In the acylation of 2-phenyl-2-propanol with either benzoyl or pivaloyl chloride, **1**, **2**, and **3** are more effective than DMAP [complete experimental].

T. Kamijo, R. Yamamoto, H. Harada, and K. Iizuka, Chem. Pharm. Bull., **31**, 3724-3727 (1983).

Trimethylsilylchlorochromate: A New Chromium VI Oxidant



$CrO_3 + Me_3SiCl$
$K_2CrO_4 + 3\ Me_3SiCl$
$K_2Cr_2O_7 + 4\ Me_3SiCl$
$\longrightarrow Me_3SiO\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-Cl$

1

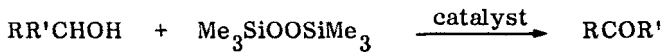
$RR'CHOH + \mathbf{1} \longrightarrow RCOR'$

R	R'	Time (min)	Yield (%)
Ph	H	45	81
Ph	Ph	20	98
O_2NPh	H	210	87
$-(CH_2)_5-$		50	88

Primary and secondary alcohols are readily and cleanly oxidized to aldehydes and ketones upon treatment with dichloromethane solutions of chromium trioxide/chlorotrimethylsilane (1:1), potassium chromate/chlorotrimethylsilane (1:3), or potassium dichromate/chlorotrimethylsilane (1:4). The active species is proposed to be trimethylsilylchlorochromate (**1**). Attempted isolation of **1** resulted in a violent explosion during distillation. Unlike other chromium VI oxidants, only 1:1 molar ratios of **1**/alcohol are needed to obtain aldehydes and ketones in high yield in short reaction times [partial experimental].

J. M. Aizpurna, C. Palomo, and E. Herriko, Tetrahedron Lett., **24**, 4367-4370 (1983).

Transition Metal - $Me_3SiOOSiMe_3$ Oxidation of Alcohols



$RR'CHOH + Me_3SiOOSiMe_3 \xrightarrow{\text{catalyst}} RCOR'$

1

Catalytic amounts of pyridinium dichromate in the presence of excess bis(trimethylsilyl)peroxide (**1**) oxidizes primary and secondary alcohols to aldehydes and ketones in good to excellent yields (71-100%) at room temperature. The **1**, dichromate, and alcohol are used in a 3.0:0.1:1.0 molar ratio. Chromium trioxide and pyridinium chlorochromate are much less effective than pyridinium dichromate.

Catalytic amounts of dichlorobis(triphenylphosphine)ruthenium (II) in the presence of excess **1** readily and selectively oxidize primary alcohols to aldehydes. Yields are good to excellent with allylic alcohols and fair to good with other primary alcohols when **1**, ruthenium, and alcohol are used in a 2.0:0.05:1.0 molar ratio. Competitive studies between primary allylic and secondary alcohols gave 95/6 to 99/3 (% yield) ratios of aldehydes/ketones, and diols containing both primary allylic and secondary alcohols gave hydroxy aldehydes in good yield [partial experimental].

S. Kanemoto, K. Oshima, S. Matsubara, K. Takai, and H. Nozaki, Tetrahedron Lett., **24**, 2185-2188 (1983).
