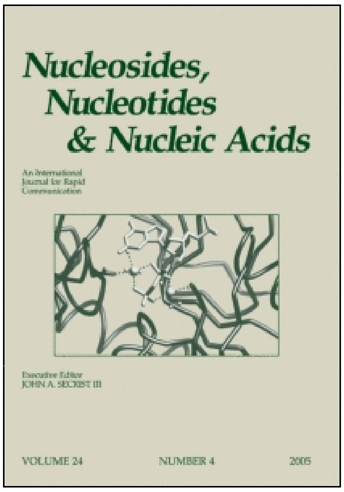

Nucleosides, Nucleotides and Nucleic Acids

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Nuclbosidest/tides Abstracts

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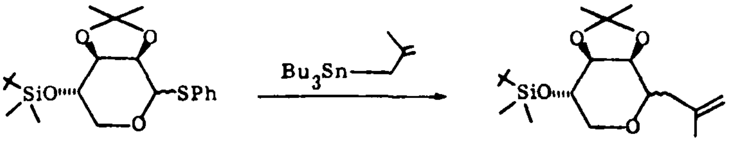
NUCLEOSIDES & NUCLEOTIDES, 3(4), 441-443 (1984)

NUCLEOSIDES/TIDES ABSTRACTS

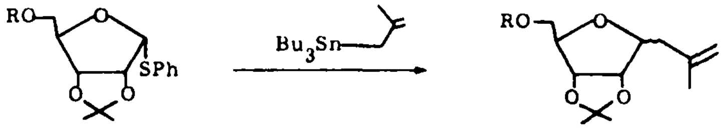
Compiled by Dr. Marshall W. Logue, Michigan Technological University

New Highly Stereoselective Synthesis of C-Glycosides



1 2

hν, 87%, α:β (92:8)
Bu_3SnOTf, 95%, α:β (1:99)



3 4

R = $PhCH_2OCH_2$, Bu_3SnOTf, 80%, α:β (1:99)
R = $tBu(Ph)_2Si$, hν, 86%, α:β (17:83)
R = $tBu(Ph)_2Si$, Bn_3SnOTf, 96%, α:β (54:16)
R = $tBuMe_2Si$, hν, 79%, α:β (40:60)
R = $tBuMe_2Si$, Bn_3SnOTf, 91%, α:β (59:41)

L-Lyxose thioglycoside **1** reacts with methallyltributylstannane under photochemical initiation to give an anomeric mixture of **2** in which the α anomer greatly predominates. Lewis acid initiation with tributylstannyl triflate of the same reaction produces a mixture of the same anomers, but with the opposite (predominantly β anomer) stereoselectivity. Similar results were found in the ribose series **3**, but the stereoselectivity varied greatly depending

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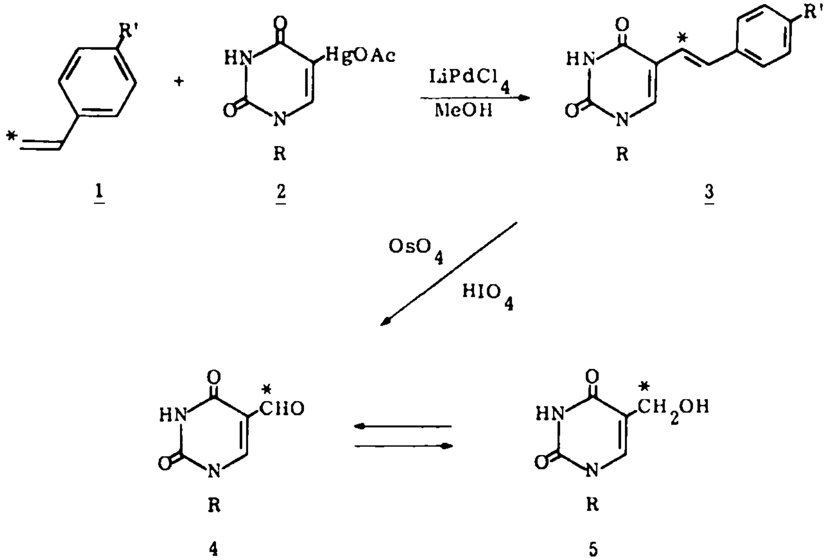
upon the nature of the 5-O-substituent. The photochemical route is not useful with the benzyloxymethyl group because significant amounts (50%) of byproducts are generated. The 2,3:5,6-di-O-isopropylidene-D-mannoside also exhibits high stereoselectivity (99:1 by hν versus 1:99 by triflate); however, glucopyranosides gave 1:1 mixtures of anomers with both photochemical and Lewis acid initiation [partial experimental].

G. E. Keck, E. J. Enholm, and D. F. Kachensky, Tetrahedron Lett., **25**, 1867-1870 (1984).

Convenient Route to Isotopically Labelled 5-Substituted Uracil Nucleotides



R = 2-deoxyribose-5-phosphate; R' = H, NO$_2$;
* = ^{14}C, ^{13}C

A number of singly or doubly-labelled 5-substituted uracil nucleotides are readily available via the palladium-catalyzed coupling of styrenes **1** with the 5-mercuriacetate derivative **2**. Use of [^{14}C] - or [B$_c$]-labelled **1** allows the ready synthesis of 5-substituted uracil nucleotide derivatives containing either [^{14}C] - or [^{13}C]-labelled one-carbon units in any of four possible oxidation states [-CHO, -CH$_2$OH, CO$_2$H, or CH$_3$). The reduction of [^{14}C] - or [^{13}C] - labelled **4** with labelled sodium borohydride gives the doubly-labelled derivative **5**, which upon further reduction or subsequent reoxidation leads to the other oxidation states of the doubly-labelled derivative **5**. Although the authors discuss only tritium double-labelling, deuterium double-labelling could likewise be accomplished [partial experimental].

J. S. Park, C. F. Bigge, M. B. Hassan, L. Maggiora, and M. P. Mertes, J. Chem. Soc., Chem. Commun., 553-554 (1984).

Efficient Catalyst for t-Butyldimethylsilylation

$$\mathrm{ROH + t\text{-}BuMe_2SiCl \xrightarrow{(i\text{-}Pr)_2NEt} t\text{-}BuMe_2SiOR}$$

R = primary, secondary, tertiary alkyl

Diisopropylethylamine (DIPEA) is a very effective catalyst for the silylation of alcohols with t-butyldimethylchlorosilane. Advantages of DIPEA over previously used catalysts are its poor nucleophilicity, its volatility, and rapid rates of reaction in either dichloromethane or dimethylformamide (DMF), DIPEA catalyzed silylations occur much faster in DMF than in dichloromethane; in fact, primary alcohols react exothermically in DMF. Primary, secondary, and hindered secondary alcohols are silylated in excellent yield (84-100%) at room temperature after 1-6h (CH_2Cl_2) or 10 min-1.5h (DMF). Even the tertiary alcohol linalool is silylated in 53% yield after 40h at 100°C [partial experimental].

L. Lombardo, Tetrahedron Lett., **25**, 227-228 (1984).