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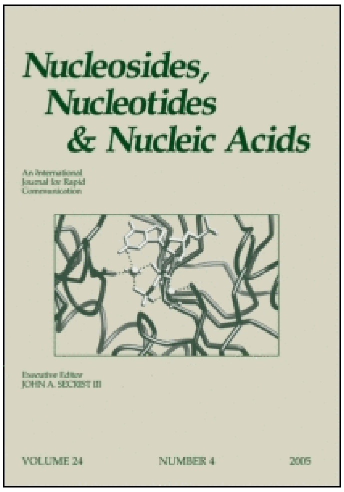

Nucleosides, Nucleotides and Nucleic Acids

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Nucleosides/Tides Abstracts

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NUCLEOSIDES & NUCLEOTIDES, 5(4), 457-460 (1986)

NUCLEOSIDES/TIDES ABSTRACTS

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

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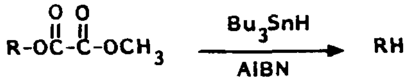
Deoxygenation of Tertiary and Secondary Alcohols via Their Methyl Oxalyl Esters



$$R\text{-}O\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3 \xrightarrow[\text{AIBN}]{Bu_3SnH} RH$$

Secondary and tertiary alcohols may be deoxygenated by treatment of their derived methyl oxalyl esters with tributylstannane and azobisisobutyronitrile (AIBN) in toluene under reflux. Methyl oxalyl esters of primary alcohols do not deoxygenate under these conditions, but predominantly regenerate the primary alcohols.

The requisite methyl oxalyl esters are readily prepared from the secondary and tertiary alcohols either by reaction at room temperature with oxalyl chloride in an aprotic solvent followed by methanolysis or by reaction with methyl oxalyl chloride under reflux in an aprotic solvent (e.g., THF). Hindered alcohols, for which difficulty in forming thiocarbonates, thiobenzoates, or O-phenylthiocarbonates is encountered, form methyl oxalyl esters with surprising ease [No Experimental].

S. C. Dolan and J. MacMillan, J. Chem. Soc., Chem. Commun., 1588-1589 (1985).

A New Homogeneous Desulfurization Reagent: Nickelocene-Lithium Aluminum Hydride

Nickelocene reacts with lithium aluminum hydride in a 1:1 mole ratio to form a homogeneous organonickel compound that reductively desulfurizes

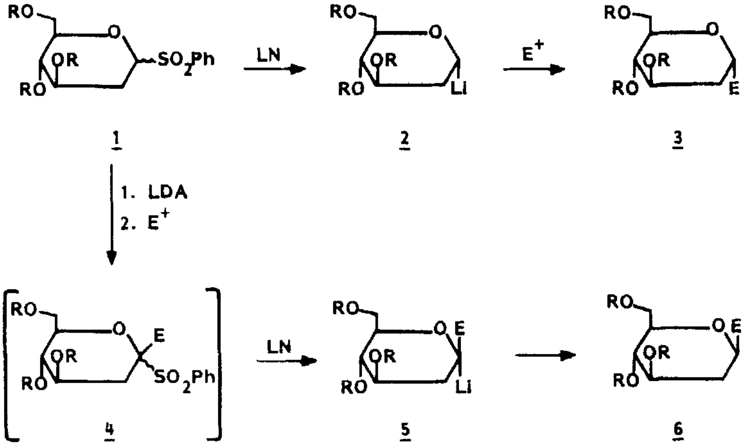
0732-8311/86/0504-0457$3.50/0

thiols, sulfides, and thioacetals. Most sulfur-containing compounds are reductively desulfurized in moderate to good yield (see below). Benzylic, α-acyl, or aryl C-S bonds are cleaved fairly easily (14-16 h at room temperature), whereas simple alkyl C-S bonds require more drastic conditions (16 h at reflux). Each C-S bond requires one equivalent of the nickelocene-$LiAlH_4$ reagent. Ester, ketone, and alkene functions are not reduced by the reagent, but nitro functions are reduced to amines [Partial Experimental].

2-Naphthylmethanethiol (2-methylnaphthalene, 80%)
Dibenzothiophene (biphenyl, 70%)
2-Naphthalenethiol (naphthalene, 74%)
9,9-Ethylenedithiofluorene (fluorene, 55%)
1-Decanethiol (Decane, 41%)

M.-C. Chan, K.-M. Cheng, M. K. Li, and T.-Y. Luh, J. Chem. Soc., Chem. Commun., 1610-1611 (1985).

Highly Stereoselective Syntheses of C-Glycosides via Phenylsulfonyl Glycosides

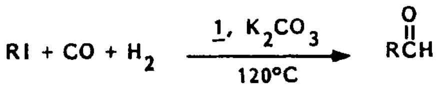


a, R = $tBuMe_2Si$
b, R = $PhCH_2$
c, R = Me
$E^+ = D_2O$, RX,
RCHO

The phenylsulfonyl glycosides **1a-c** are readily available from 3,4,6-tri-O-acetyl-, 3,4,6-tri-O-benzyl-, and 3,4,6-tri-O-methyl-D-glucals in 83, 77, and 75% yields, respectively. Reductive lithiation of **1** with lithium naphthalenide (LN) at -78 °C gives the configurationally stable glycosyllithium **2**, which reacts with electrophiles to give exclusively the β-C-glycosides **3**. Alternatively, deprotonation of **1** with lithium diisopropylamide (LDA) followed by reaction with electrophiles gives unstable **4** (α:β ratio, 4), which upon in situ reductive lithiation produces the configurationally stable glycosyllithium **5**. Protolysis of **5** gives exclusively the β-C-glycosides **6**. Pyridinium chlorochromate oxidation of alcohols derived from alkylations of **2** or **5** with aldehydes gives the corresponding ketones with complete retention of configurations. When esters are used as electrophiles with **5**, the resulting acyl glycosides are predominantly the α-anomers (10:1-20:1, α:β ratios) [Partial Experimental].

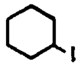
J.-M. Bean and P. Sinay, Tetrahedron Lett., **26**, 6185-6189, 6189-6192, 6193-6196 (1985).

Carbonylations of β-Hydrogen-Containing Organic Halides via Organoplatinum Catalysis



$$RI + CO + H_2 \xrightarrow[120°C]{1,\ K_2CO_3} R\overset{O}{\overset{\|}{C}}H$$

$$RI + CO + CH_3OH \xrightarrow[120°C]{1,\ K_2CO_3} RCO_2CH_3$$

	aldehyde	ester
$n\text{-}C_6H_{13}I$	86%	79%
$n\text{-}C_6H_{13}CH(Me)I$	51%	76%
	78%	74%

Dichlorobis(triphenylphosphine)platinum (II) (**1**) serves as a catalyst for carbonylations of organic iodides. Organic iodides react with carbon monoxide and hydrogen in the presence of **1** and potassium carbonate to produce aldehydes, whereas esters are produced when methanol is substituted for hydrogen. These reactions occur even with organic iodides which contain β-hydrogens on sp^3 hybridized carbons. This is contrary to palladium-catalyzed carbonylations of organic halides which fail when β-hydrogens on sp^3 hybridized carbons are present because of facile dehydridopalladation [Partial Experimental].

R. Takeuchi, Y. Tsuji, and Y. Watanabe, J. Chem. Soc., Chem. Commun., 351-352 (1986).