A Novel Method for the Deoxygenation of Acetylated Sugars

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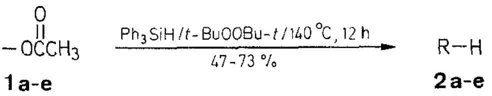
The conversion of acetylated surgars **1** to deoxy sugars **2** by the action of triphenylsilane under homolytic conditions is reported. Both furanoses and pyranoses bearing an acetylated primary or secondary alcohol are effectively deoxygenated.

Deoxygenation of sugars occupies a significant position in carbohydrate chemistry.[1] Although there have been numerous methods for the deoxygenation via various intermediates,[2-7] reports of satisfactory methods for the deoxygenation of acetylated sugars, which were often utilized in sugar chemistry, are rare.[8] We have recently reported the reductive deoxygenation of esters to the corresponding hydrocarbons using triphenylsilane.[9] The fact that the hydrocarbons were obtained in high yield prompted us to apply the reaction to the preparation of deoxysugars.



$$R-O\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[47-73\ \%]{Ph_3SiH/t\text{-}BuOOBu\text{-}t/140\,°C,\ 12\ h} R-H$$

1a-e **2a-e**

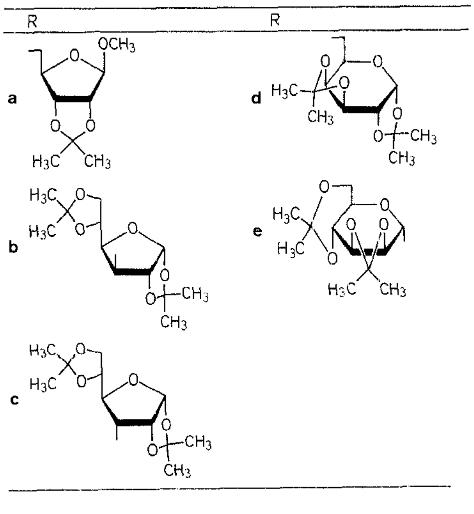


Table. Reductive Deoxygenation of Sugars

ROAc	RH	Yield (%)	bp (°C)/Torr[a]	Molecular Formula[b] or Lit. bp (°C)/Torr	$[\alpha]_D^{18}$ (*c*, $CHCl_3$); Lit. $[\alpha]_D$ (*c*, solvent)	^1H-NMR (CCl_4/TMS)[d] δ, *J* (Hz)
1a[12]	**2a**	71	150–155/80	66/9[10]	−98.0° (1); −109° (2, EtOH)[10]	1.25 (d, 3H, *J* = 7); 1.3 (s, 3H); 1.4 (s, 3H); 3.3 (s, 3H); 4.25 (q, 1H, *J* = 7); 4.35 (d, 1H, *J* = 6); 4.5 (d, 1H, *J* = 6); 4.8 (s, 1H)
1b[13]	**2b**	66	150–155/40	74–78/0.3[11]	−9.0° (2); −5.78° (4.2, EtOH)[11]	1.25 (b s, 6H); 1.35 (s, 3H); 1.45 (s, 3H); 1.9–2.3 (m, 2H); 3.6–4.25 (m, 4H); 4.65 (t, 1H, *J* = 4); 5.7 (d, 1H, *J* = 4)
1c[14]	**2c**	47	170–175/75	74–78/0.3[11]	−8.5° (1.5); −5.78° (4.2, EtOH)[11]	1.25 (b s, 6H); 1.35 (s, 3H); 1.45 (s, 3H); 1.9–2.3 (m, 2H); 3.6–4.25 (m, 4H); 4.65 (t, 1H, *J* = 4); 5.7 (d, 1H, *J* = 4)
1d[15]	**2d**	70	150–155/20	–[c]	−49.0° (1.4); −53.1° (6.4, $CHCl_3$)[8]	1.15 (d, 1H, *J* = 6); 1.3 (b s, 6H); 1.4 (s, 3H); 1.45 (s, 3H); 3.75 (m, 1H); 3.95 (dd, 1H, *J* = 8, 2); 4.15 (dd, 1H, *J* = 5, 2); 4.45 (dd, 1H, *J* = 8, 2); 5.35 (d, 1H, *J* = 5)
1e[e]	**2e**	73	165–170/22	$C_{12}H_{20}O_5$ (244.3)	−136.0° (0.25)	1.3 (b s, 6H); 1.5 (b s, 6H); 2.4–3.05 (m, 2H); 3.3–3.85 (m, 4H); 3.9–4.3 (m, 2H)

[a] Kugelrohr distillation.

[b] Satisfactory microanalysis obtained: C ±0.08, H ±0.05.

[c] Structure confirmed by comparison of spectral data with those reported.[8]

[d] Recorded on a Varian EM-360 spectrometer.

[e] mp 144–146°C (hexane). Satisfactory microanalysis obtained: C ±0.06, H ±0.09. The corresponding alcohol was prepared according to the method reported.[16]

The deoxygenation was achieved by the treatment of *O*-acetyl sugars **1a**–**1e** with triphenylsilane (4 equiv) in the presence of di-*tert*-butyl peroxide (2 equiv) as a radical initiator at 140°C for 12 h (Scheme). The table shows the results. Both *O*-acetylfuranoses and pyranoses could be deoxygenated in good yield, though the deoxysugar was obtained in a somewhat lower yield in the case of allofuranose **1c**, in which attack of the silyl radical seemed to be sterically prevented owing to the neighboring bulky groups. It is noteworthy that 1-*O*-acetyl-2,3:4,6-di-*O*-isopropylidene-α-D-mannopyranose (**1e**) was also deoxygenated effectively, although the free anomeric hydroxy compound was recovered upon photolysis of **1e**.[8]

The present method offers a new approach to the preparation of deoxysugars. However, difficulties in the separation of deoxysugars from the reaction mixtures may arise in the case of high boiling sugars such as oligosaccharides. Further studies to overcome these difficulties are in progress.

Methyl 5-Deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (2a); Typical Procedure:

A mixture of methyl 5-*O*-acetyl-2,3-*O*-isopropylidene-β-D-ribofuranoside (**1a**; 300 mg, 1.3 mmol), triphenylsilane (1.33 g, 5.1 mmol), and *t*-BuOOBu-*t* (375 mg, 2.6 mmol) is heated in a sealed tube at 140°C for 12 h. Direct distillation of the reaction mixture gives pure **2a** (Table). Also prepared were 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2b**), 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**2c**), 6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**2d**), and 1-deoxy-2,3:4,6-di-*O*-isopropylidene-D-mannopyranitol (**2e**).

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