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Stereoselective Reduction of 3-*O*-Hexofuranosyl *S*-Methyl Dithiocarbonates with Tributyltin Deuteride

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Summary The reduction of several 3-*O*-hexofuranosyl (*gluco, allo, galacto*) *S*-methyl dithiocarbonates with tributyltin deuteride leads to highly stereoselective syntheses of 3-deoxy-3-deuterio-hexofuranoses.

The reduction of *O*-alkyl *S*-methyl dithiocarbonates with tributyltin hydride has been used for the efficient deoxygenation of secondary alcohols to alkanes[1] [equation (1)]

$$R_2CHOH \rightarrow R_2CHOC(S)SMe \rightarrow R_2CH_2 + COS + Bu_3SnSMe \qquad (1)$$

and for the conversion of some 1,2:5,6-di-*O*-isopropylidene-α-D-hexofuranoses into their 3-deoxy derivatives, *e.g.*, (**1**) into (**2**)[1] and (**3**) into (**4**).[2] This communication describes the corresponding reduction of some dithiocarbonates with tributyltin deuteride to provide novel, stereoselective syntheses of 3-deoxy-3-deuterio-derivatives, *e.g.*, (**5**) and (**6**). Delivery of the deuterium atom in a radical process[1] to the *exo* face of these bicyclic systems is expected from results previously obtained in comparable nucleophilic reactions.[3]

In a typical experiment, tributyltin deuteride† (1 mmol) was added to the dithiocarbonate (1 mmol) in refluxing toluene (15 ml), the reaction mixture was heated to reflux for 12 h, and more deuteride (1 mmol) was added with further reflux for 6 h. Work-up and chromatography,[1] followed by either recrystallisation or distillation under reduced pressure, gave the 3-deoxy-3-deuterio-compounds. The stereoselectivity of the various reductions was then determined from an analysis of the proton, carbon, and deuterium n.m.r. spectra for positions 2 and 3 in the furanose ring (see Table).

Table. N.m.r. data for 3-deoxy-hexofuranoses (^1H, 270 MHz, first order analysis), (^{13}C, 67·89 MHz, proton decoupled), and (^2H, 44·14 MHz, proton decoupled). Chemical shifts (δ) are in p.p.m. relative to internal Me_4Si.

	H-2	*Exo*-^{1}H-3		*Endo*-^{1}H-3			^{2}H-3
Compound	$J_{1,2}$/Hz	δ	$J_{2,3}$/Hz	δ	$J_{2,3}$/Hz	C-3	δ
(**2**)[a,b]	dd, 3·5	1·72	ddd, 5·0	2·18	dd, 0·0	s(δ 35·61)[d]	—
(**5**)	d, 3·5		—		d br, 0·0	t	1·73
(**8**)[a]	dd, 3·5		br, 5·0		—	t	2·17
(**11**)	d, 3·5		—		—	br	2·16 1·74
(**4**)[b,c]	ddd, 4·0	2·20	ddd, 6·0	1·82	ddd, 1·5	s(δ 33·65)	—
(**6**)[b]	dd, 4·0		—		br, 1·5	t	2·19

[a] Ref. 4. [b] S. A. Black, L. D. Hall, K. N. Slessor, and A. S. Tracey, *Canad. J. Chem.*, 1972, **50**, 1912. [c] Ref. 2. [d] W. A. Szarek, A. Zamojski, A. R. Gibson, D. M. Vyas, and J. K. N. Jones, *Canad. J. Chem.*, 1976, **54**, 3783.

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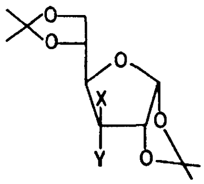
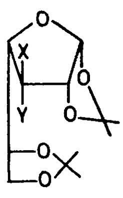
† Prepared (ref. 1) by the reduction of tributyltin chloride with lithium aluminium deuteride (99 atom %).



	X	Y
(**1**)	OH	H
(**2**)	H	H
(**5**)	D	H
(**7**)	OCS$_2$Me	H
(**8**)	H	D
(**9**)	H	OCS$_2$Me
(**10**)	D	OCS$_2$Me
(**11**)	D	D



	X	Y
(**3**)	OH	H
(**4**)	H	H
(**6**)	D	H
(**12**)	OCS$_2$Me	H
(**13**)	H	OCS$_2$Me
(**14**)	D	OCS$_2$Me

The reduction of the D-*gluco*-dithiocarbonate (**7**)[1] with tributyltin deuteride gave a mixture of compounds (**5**) and (**8**) in the ratio of 85:15(±5). The stereochemical course of the reduction was obtained from the ^{1}H n.m.r. spectrum of the mixture (*exo*-H-3 almost absent; H-2 mainly a doublet, $J_{1,2}$ 3·5, $J_{2,\,endo\text{-}3}$ 0·0 Hz[4]), and a measure of the stereoselectivity was obtained from the ^{2}H n.m.r. spectrum by integration. The reduction of the D-*allo*-dithiocarbonates (**9**)[2] and (**10**)‡ with the deuteride and the hydride, respectively, again gave mixtures of compounds (**5**) and (**8**) [85:15 for compound (**9**) and 15:85 for compound (**10**)]. The reduction of compound (**10**) with the deuteride gave compound (**11**), showing two equally intense signals in the ^{2}H n.m.r. spectrum.

The reduction of the D-*galacto*-dithiocarbonate (**12**)[2] with the deuteride gave only compound (**6**). Initial experiments for the reduction of the D-*gulo*-dithiocarbonates (**13**) and (**14**) have shown the same high stereoselectivity.

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‡ Prepared using the lithium aluminium deuteride instead of sodium borodeuteride (ref. 4).

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[3] D. C. Baker, D. Horton, and C. G. Tindall, Jr., *Methods in Carbohydrate Chem.*, 1976, **7**, 3; J. S. Brimacombe, P. A. Gent, and M. Stacey, *J. Chem. Soc.* (*C*), 1968, 567.

[4] C. R. Haylock, L. D. Melton, K. N. Slessor, and A. S. Tracey, *Carbohydrate Res.*, 1971, **16**, 375.