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Note

Bis(organo)mercury compounds by methoxymercuration of enolic sugar derivatives*

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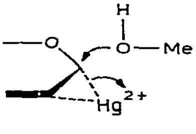
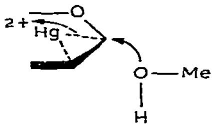
Methoxymercuration[2] with mercury(II) acetate in methanol is a convenient method for the preparation of methyl 2-deoxy-glycosides from glycals and glycal acetates[2]. The reactions yield isomeric mixtures which are derived from regioselective, nucleophilic ring-opening of the mercurinium intermediates A and B by methanol. The stereoselectivity of the initial addition of mercury depends on the kind of substituent attached to C-3 of the pyranoid ring[3]. Bis(organo)mercury compounds, formed by subsequent reaction of the 1:1 product of methoxymercuration with an excess of the glycal have never been observed[2]. In the case of the otherwise highly reactive glycals, the reaction of the primary adduct may be prevented by steric hindrance, as ethyl vinyl ether yields a bis(organo)mercury compound[4]. Recently, Ferrier and Prasit[5] showed that a 6-deoxyhex-5-enopyranoside also yields, exclusively, the 1:1 adduct by the standard methoxymercuration method. Only under more drastic conditions, with phenylmercury acetate as the reagent, could the 1:2 adduct, a bis(glycos-6-yl)mercury compound, be obtained. Methoxymercuration of the exocyclic double bond occurred stereospecifically in both instances, most probably giving an axially oriented methoxyl group at the anomeric site newly formed. These results are consistent with our findings[6].



A



B

Four enolic sugar derivatives having readily accessible, exocyclic double bonds, namely, methyl 3,4,5-tri-*O*-acetyl-2,6-anhydro-7-deoxy-D-*gulo*-[7] (**1**) and -L-*manno*-hept-6-enoate[7] (**2**), as well as 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-1-deoxy-D-

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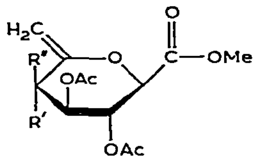
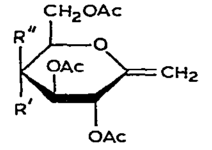
*Reactions of Enolic Sugar Derivatives, Part XV. For Part XIV, see ref. 1.

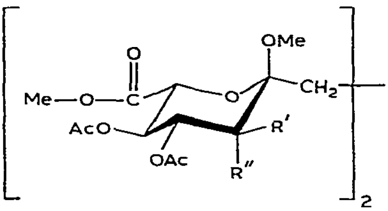


1 R′ = OAc, R″ = H
2 R′ = H, R″ = OAc

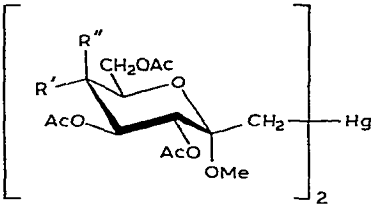


3 R′ = OAc, R″ = H
4 R′ = H, R″ = OAc

gluco-[8] (3) and -D-*galacto*-hept-1-enitol[9] (4) reacted readily at room temperature with a molar excess of mercury(II) acetate in methanol. After a few minutes, t.l.c. with 4:1 benzene–methanol as the solvent showed, in each case, besides the polar, 1:1 adducts expected, one nonpolar component (5–8). The nonpolar components increased at the expense of the polar products on adding more unsaturated substrate. A molar ratio of the substrate to mercury(II) acetate of 2:1 yielded, almost quantitatively, the nonpolar products, which were all obtained crystalline after evaporation of the reaction mixture. The elemental analyses, especially, indicated that the nonpolar products are bis(organo)mercury compounds (see Table I).



5 R′ = OAc, R″ = H
6 R′ = H, R″ = OAc



7 R′ = OAc, R″ = H
8 R′ = H, R″ = OAc

TABLE I

PROPERTIES OF COMPOUNDS 5–8

Starting material	*Product*	*Properties of the product*					
		Yield (%)	*Analysis for*	*Calc.*	*Found*	$[\alpha]_{578}^{22}$ *(degrees)*[a]	*M.p. (degrees)*[b]
1	5	80	$C_{30}H_{42}HgO_{20}$	C, 39.03 H, 4.58	39.13 4.86	−42.8	138
2	6	80			39.08 4.75	−12.2	143
3	7	74	$C_{32}H_{46}HgO_{20}$	C, 40.40 H, 4 87	40.51 5.03	+43.8	123
4	8	80			40.31 4.85	+63 5	153

[a]For specific rotations, *c* 1.0 ($CHCl_3$). [b]Compounds 5–8 all showed ν_{max}^{KBr} 1740 cm^{-1} (OAc).

For compound **6**, the α configuration of the anomeric carbon atom and the axial disposition of the methoxyl group were determined by X-ray-diffraction analysis[6]. For compounds **7** and **8**, the α configuration at C-2 was established by comparison of their ^{1}H- and ^{13}C-n.m.r. spectra (for data, see Tables II and III) with the spectra of the corresponding heptulosides, whose configurations have been unequivocally established[9]. Finally, the configuration for **5** can be deduced by comparison of the n.m.r. spectra of **5** and **7**. Thus, X-ray analysis, together with configurational correlation by n.m.r. measurements, proved that the four compounds are bis[methyl (methyl 3,4,6-tri-*O*-acetyl-1-deoxy-α-L-*gluco*-heptulosid)uronate-1-yl]mercury(II) (**5**), bis[methyl (methyl 3,4,6-tri-*O*-acetyl-1-deoxy-α-L-*manno*-heptulosid)uronate-1-yl]-mercury(II) (**6**), bis(methyl 3,4,5,7-tetra-*O*-acetyl-1-deoxy-α-D-*gluco*-heptulosid-1-yl)mercury(II) (**7**), and bis(methyl 3,4,5,7-tetra-*O*-acetyl-1-deoxy-α-D-*galacto*-heptulosid-1-yl)mercury(II) (**8**).

TABLE II

^{1}H-CHEMICAL-SHIFTS[a] AND COUPLING CONSTANTS[b] OF COMPOUNDS 5–8 IN $CDCl_3$ SOLUTION

H atoms	*Compound*			
	5	**6**	**7**	**8**
	δ			
1	1.48	1.44	1.44	1.40
1′	1.34	1.39	1.31	1.40
3	5.14	5.23	5.10	5.26
4	5.49	5.50	5.46	5.32
5	5.33	5.34	5.16	5.44
6	4.13	4.10	3 82	4.01
7,7′	—	—	4.22, 4.12	4.11, 4.11
OCH_3	3.32	3.36	3.29	3.31
$COOCH_3$	3.75	3.74	—	—
CH_3CO-	2 11	2.21	2.12	2.15
	2.01	2.02	2.09	2.15
	1.98	1.97	2.02	2.05
	—	—	1.98	1.95
	J (i,j)			
1,1′	13.5	13.5	13.5	13.5
3,4	9.5	3.5	9.5	10.5
4,5	9.5	10.5	9.5	3.5
5,6	10.0	10.0	10 0	1.5
6,7	—	—	5.5	7.0
6,7′	—	—	2.5	7.0
7,7′	—	—	12.5	[c]

[a] δ values in p.p.m- (±0.1 p p m.) at 360 MHz; internal standard, Me_4Si; concentration, 10 mg.mL^{-1}. [b] In Hz (±0.3 Hz), as determined by first-order analysis of the 360-MHz spectrum. No satellites due to coupling of protons with ^{199}Hg could be observed. [c] Not obtainable by first-order analysis.

TABLE III

^{13}C-CHEMICAL SHIFTS^a OF COMPOUNDS 5–8 IN $CDCl_3$ SOLUTION

C atom	*Compound*			
	5	**6**	**7**	**8**
1	41.55	41.21	41.95	42.54
2	104.77	105.29	104.05	104.56
3	75.09	72.43	75.55	72.94
4	70.68	69.48	71.30	68.97
5	69.89	66.57	69.08	68.33
6	69.89	70.93	68.93	67.84
7	168.34	168.49	62.64	61.83
OCH_3	47.95	48.22	47.54	47.73
$COOCH_3$	52.76	52.74	—	—
-$COOCH_3$	170.21	170.57	170.75	170.42
	170.08	169.86	170.32	170.23
	169.52	—	170.17	170.00
	—	—	169.67	—
CH_3CO-	20.77	20.97	20.87	21.00
	20.66	20.71	20.85	20.74
	20.60	—	20.70	20.64
	—	—	20.64	—

$^a\delta$ values in p.p.m. (±0.02 p.p.m.) at 90.53 MHz; internal standard, Me_4Si; concentration, 100 mg mL^{-1}; temperature 30°. Satellites due to coupling of ^{13}C nuclei with ^{199}Hg could only be observed as broad doublets ($\Delta\ \nu(\frac{1}{2})$ ~30 Hz) for the signals of C-1 ($J_{C\text{-}1,Hg}$ ~820 Hz).

EXPERIMENTAL

General. — Melting points are uncorrected. T.l.c. was performed on silica gel F_{254} (Merck). Detection was effected by charring with sulfuric acid. I.r. spectra were recorded with a Perkin–Elmer 137 Infracord spectrometer, and optical rotations with a Perkin–Elmer 141 polarimeter. N.m.r. spectra (^1H and ^{13}C) were recorded in the Fourier-transform mode with a Bruker HX-360 spectrometer. The assignments of ^1H- and ^{13}C-n.m.r. signals were established by homonuclear and heteronuclear decoupling experiments.

General procedure. — The unsaturated compound (**1**, **2**, **3**, or **4**) (1.0 mmol) in dry methanol (5 mL) was stirred, and then mercury(II) acetate (0.55 mmol) was added. After dissolution had occurred, the solution was kept for 3 h at room temperature, and evaporated to dryness, to yield, normally, crystalline product. If crystallization did not occur spontaneously, it was found advisable to purify the residue by flash chromatography[10] on silica gel, using 4:1 (v/v) benzene–methanol as the solvent. The products (**5**, **6**, **7**, or **8**) were all recrystallized from ether.

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