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Preliminary communication

ORGANOMETALLIC DERIVATIVES OF SUGARS

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Summary

Stable organometallic derivatives of glucose were prepared either by treatment of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose with organometallic hydroxides R_3MOH and oxides R_2MO or by the reaction between 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide with R_3SnSLi.

Recently there have been a few reports [1—4] of organotin derivatives of sugars. Although some carboxylate derivatives have been described [4], most of the compounds prepared are alkoxides, in which hydrogen atoms of sugar OH groups are replaced by tin, and in general are readily hydrolysed. We now report particularly stable sugar derivatives in which the organometallic group is linked via sulphur.

Two synthetic procedures were used (Scheme 1). In route A 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (I) was converted to 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (II) by successive treatment with thiourea

TABLE 1

ANALYTICAL DATA ON ORGANOMETALLIC DERIVATIVES OF 2,3,4,6-TETRA-*O*-ACETYL-1-THIO-β-D-GLUCOPYRANOSE (III AND IV) AND OF 1-THIO-β-D-GLUCOSE (V)

Compound		M.p. (°C)	Analyses: Found (calcd.) (%)		
			C	H	S
III M = Sn, R = Ph	($C_{32}H_{34}O_9SSn$)	44—46	53.5 (53.9)	4.65 (4.8)	4.7 (4.5)
III M = Sn, R = Bu	($C_{26}H_{46}O_9SSn$)	33—35	47.65 (47.8)	6.9 (7.1)	—
III M = Ge, R = Ph	($C_{32}H_{34}O_9GeS$)	35—39	57.6 (57.6)	5.1 (5.1)	—
III M = Pb, R = Ph	($C_{32}H_{34}O_9PbS$)	50—53	47.7 (47.9)	4.3 (4.3)	4.0 (4.0)
IV M = Sn, R = Bu	($C_{36}H_{56}O_{18}S_2Sn$)	58—63	45.0 (45.0)	5.8 (5.9)	6.8 (6.7)
V M = Sn, R = Ph	($C_{24}H_{26}O_5SSn$)	glass	53.1 (52.9)	5.2 (4.8)	5.6 (5.9)
V M = Sn, R = Bu	($C_{18}H_{38}O_5SSn$)	glass	43.5 (44.5)	7.4 (7.9)	6.4 (6.6)

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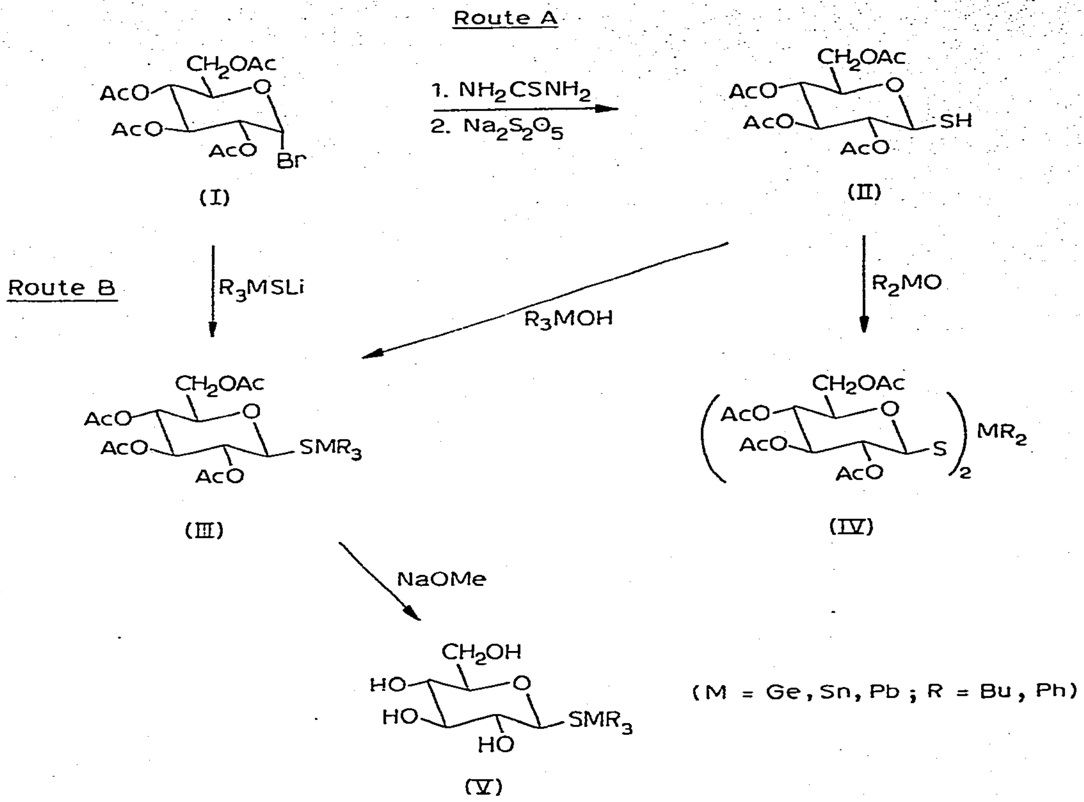
SCHEME 1



and sodium metabisulphite [5]. Reaction between II and the organometallic hydroxide R_3MOH or oxide R_2MO (M = Sn, Pb or Ge) gave the acetylated organometallic sugar derivatives III and IV. Some of these compounds could also be prepared by route B in which I was treated directly with R_3SnSLi prepared by reaction between the organotin lithium compound and sulphur in THF [6]. Organotin derivatives of free glucose (V) were obtained by deacetylation using sodium methoxide.

The compounds prepared are listed in Table 1 together with some analytical data. The infrared and NMR spectra showed the expected absorption bands.

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