

HEXOSE SULPHITES AND ARSENITES: THEIR SYNTHESIS AND HYDROLYSIS

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AS PART of an investigation of the sugar esters of the Group V and VI oxyacids, we have had occasion to synthesise sulphite and arsenite esters of hexitols and hexoses, and to examine their behavior on hydrolysis.

Cyclic sulphites exemplifying five- and six-membered rings have been synthesised, together with dihexose sulphites. Only cyclic arsenites have so far been obtained. While the sulphite esters were moderately stable, the arsenites were rapidly decomposed in the presence of moisture and the determination of structure proved difficult.

The action of thionyl chloride upon methyl 2,3-di-O-methyl- α -D-glucoside in chloroform-pyridine gave I, methyl 2,3-di-O-methyl- α -D-glucoside 4,6-sulphite m.p. 133-135° $[\alpha]_D^{16.5} + 110^\circ$ (c, 0.17 in EtOH), Found: C,40.5;H,5.9;S,11.6. $C_9H_{16}O_7S$ requires C, 40.3;H,6.0;S,11.9%. as slightly hygroscopic needles, stable for several months on storage in a desiccator. Methyl 4,6-O-benzylidene- α -D-glucoside 2,3-sulphite, II, was obtained by a modification of the method of Honeyman and Morgan¹ as colorless needles, m.p. 195-198° $[\alpha]_D^{17.5} + 135^\circ$ (c, 0.9 in $CHCl_3$). By the action of thionyl chloride upon a concentrated solution of methyl 4,6-O-benzylidene- α -D-glucoside in

pyridine, di-(methyl 4,6-O-benzylidene- α -D-glucoside) sulphite III was obtained as white cubes, m.p. 207-209° $[\alpha]_D^{19} + 60^\circ$ (c, 0.7 in CHCl_3 -EtOH, 1:1), Found: C, 54.1; H, 5.9. $\text{C}_{28}\text{H}_{34}\text{O}_{13}\cdot\text{S}\cdot\text{H}_2\text{O}$ requires C, 53.5; H, 5.7%. This substance gave some methyl 3-O-acetyl-4,6-O-benzylidene- α -D-glucoside after acetylation followed by cautious acid hydrolysis, and is probably linked 2-2', assuming that no migration of the acetyl group has occurred.

The action of arsenious oxide upon glycols has been reported recently² and we have confirmed the formation of di-arsenites of mannitol and dulcitol, IV and V respectively, by the direct action of arsenious oxide in dioxane. We have applied this reaction to a number of sugars, and obtained in some cases crystalline products, apparently homogeneous, but in no case has the position of substitution been established unequivocally. Methyl- α -D-glucoside, for example, on treatment with arsenious oxide in slowly distilling dioxane, evolved the quantitative amount of water and gave white rhombs, m.p. 107-108°, $[\alpha]_D^{20} + 66.1; + 63.2$ (c, 0.598; 0.71 in CHCl_3), Found: As, 26.1; 26.6; 26.2; Molecular weight, 286. $\text{C}_7\text{H}_{13}\text{O}_7$ As requires As, 26.4%; Molecular weight, 284, and showing bands in the infra red at 2.95 (broad), 7.95, 8.25, 8.4, 8.78, 9.3, 9.7 (broad), 10.1, 11.05, 11.48, 12.4, 13.18, and 13.9 μ ..

Since 4,6-sulphites, phosphates, and phosphites are readily formed preferentially in mild conditions, from methyl- α -D-glucoside and the appropriate reagent, it is tentatively assumed that the arsenite is also the 4,6-derivative. Periodate oxidation of these derivatives is unhelpful, since there is rapid hydrolysis of the arsenite group, and reaction of the arsenious acid with the periodate. Methylation and acylation have likewise so far proved unsuccessful,

loss of arsenite again occurring.

Whilst hydrolysis of sulphate esters in alkaline conditions is well known to proceed with C-O bond fission,³ it seems generally established⁴ that in sulphite esters S-O bond fission predominates. Overend and co-workers obtained results⁵ which indicate that C-O bond fission may occur in rather different conditions.

In no case so far examined have we obtained products, which could be expected to arise as a result of C-O bond scission. The five-membered ring sulphite II hydrolysed at a rate inconveniently great for kinetic study (cf. ref. ⁶ for some similar observations upon phosphates and sulphites). The esters I and III were more conveniently studied.

Complete alkaline hydrolysis of the ester I gave methyl 2,3-di-O-methyl-4,6-O-benzylidene- α -D-glucoside as the sole carbohydrate product. Likewise, only methyl 4,6-O-benzylidene- α -D-glucoside has so far been isolated from alkaline hydrolysates of the esters II and III. Closer analysis of rates and products is proceeding.

We wished to compare the behaviour of arsenite esters with that of some analogous sugar phosphites. Since the arsenite esters are rapidly destroyed in the presence of moisture, both kinetic and structural investigation are difficult. In each case, under acidic, neutral, or basic conditions, the sole products so far identified upon hydrolysis are the parent sugar and free arsenious acid.

Thus the arsenites IV, V, and VI gave respectively mannitol, galactitol, and methyl- α -D-glucoside. The occurrence of C-O bond scission is therefore unlikely, and in this respect the arsenites and sulphites resemble the phosphites, phosphates, and selenites.

We have noted that pyrolysis of arsenite esters results in the production of arsine and oxidation products of the sugar or glycol. We are investigating the nature, and possible utility of these reactions.

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