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Abstract

Full Text

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On Certain Properties of Sugar Perchlorates and the Synthesis of O-Glycosides

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Recently, ionic reactions in the carbohydrate series have begun to attract the attention of researchers. Bredereck and co-workers, on reacting acetohalogenoses with silver perchlorate, obtained perchlorates of acetylated monosaccharides, which, in reaction with 6-trityl derivatives of sugars, form di- and trisaccharides ([1,2]). In an analogous manner, by the action of acetylated sugar perchlorates on trityl-Δ^5-pregnenol-5-ol-20 in nitromethane, the corresponding O-glycoside was obtained ([3]).

Continuing investigations on the application of perchloric acid and perchlorates in carbohydrate chemistry ([4,5]), we obtained, for the purpose of studying the properties of acetylated sugar perchlorates, the corresponding derivatives of *D*-glucose, *D*-galactose, and *D*-xylose according to the general scheme:

$$\text{[acetylated glycosyl chloride structure]} + \mathrm{AgClO_4} \longrightarrow \text{[acetylated glycosyl perchlorate structure]}^{+}\mathrm{ClO_4}^{-} + \mathrm{AgCl}$$

The acetylated perchlorates of the indicated sugars are colorless syrup-like substances, which decompose rapidly on storage with liberation of perchloric acid, partially hydrolyzing the acetyl groups of the sugar ([5]). Upon rapid heating, sugar perchlorates explode.

Taking into account the high reactivity of organic cations ([6–8]), which readily react with nucleophilic reagents, we studied the possibility of applying sugar perchlorates to the synthesis of certain sugar derivatives. We have shown that, when mixed with alcohols (methyl, ethyl, isopropyl, allyl, benzyl, and cyclohexanol), sugar perchlorates readily and in good yield form acetylated O-glycosides. Data on the glycosides obtained are given in Table 1.

Since the perchloric acid liberated in the course of the reaction destroys the product obtained (deacetylation and hydrolysis of the glycoside,

Table 1

No.	Products obtained	Solvent	Yield, %	M.p., °C, found	M.p., °C, literature data
1	β-O-Methyltetraacetyl glucoside	Methanol	78.4	104–105	104–105([9])
2	β-O-Ethyltetraacetyl glucoside	Ethanol	53.2	106	106–107([9])
3	β-O-Isopropyltetraacetyl glucoside	Propan-2-ol	54.2	134.5–135.5	134–135([9])
4	β-O-Benzyltetraacetyl glucoside	Acetone	low	96–97	96–101([12])
5	β-O-Cyclohexyltetraacetyl glucoside	Acetone	74.4	119–120	120–121([13])
6	β-O-Allyltetraacetyl glucoside	Acetone	33.5	84–86	89–90([14])
7	β-O-Methyltetraacetyl galactoside	Methanol	81.7	94	94([9])
8	β-O-Methyltriacetyl xyloside	Methanol	64.8	114–115	115([9])

as was shown chromatographically), an excess of calcium carbonate was introduced into the reaction mixture.

Although the reaction described proceeds by an ionic mechanism, the interaction of glycosyl perchlorates with alcohols has a stereospecific character. Perchlorates of *D*-glucose, *D*-galactose, and *D*-xylose form the β-anomers of acetylated O-glycosides.

By this method it was not possible to obtain the corresponding *D*-mannosides and *L*-rhamnosides. A similar result, as is known, also occurs in the synthesis of O-glycosides by the Koenigs–Knorr method ([10,11]), in the course of which cyclic orthoesters are formed for *D*-mannose and *L*-rhamnose. The mechanism of orthoester formation is explained by trans-elimination of an acetohalogenose halide

CH_3
C
O

In our case such elimination is excluded, since a carbonium cation is present in the glycosyl perchlorate. The difference in the results of O-glycoside synthesis with the obvious S_{N1} reaction mechanism is explained in this case by the different influence of the neighboring acetyl group. In the derivative of *D*-mannose it is located axially and can form a five-membered cyclic ether with the carbonium carbon, analogous to trans-elimination (I). For the equatorial acetyl group in the derivative of *D*-glucose this is impossible. The planarity of the carbocation leads to the bonds C_2—O and C_1^+—H being almost parallel (eclipsed conformation), which leads to a six-membered ring of an entirely different character (II)

(I) (II)

As a result, the glycosyl carbocation becomes accessible to attack by an alkoxide anion.

The proposed method for the synthesis of a series of acetylated O-glycosides can be used for their preparative preparation, since it makes it possible to synthesize sufficiently pure final products very rapidly (within 30–40 min).

Attempts to use this method for obtaining phenol glycosides have so far not given positive results. When pyridine is added to a freshly prepared ethereal solution of glycosyl perchlorate, quantitative precipitation of pyridinium perchlorate is observed and a mixture is formed containing a reducing sugar, chromatographically identified as an acetylated 2-oxyglycal.

Experimental Part

1. Preparation of glycosyl perchlorate. To a solution of 0.005 mole of acetohalogenose in 10 ml of absolute ether, with stirring by a magnetic stirrer, a solution of 0.005 mole of silver perchlorate in 30–40 ml of absolute ether is added dropwise over 10–15 min. The precipitate of silver chloride is separated, and the filtrate is evaporated at room temperature in the vacuum of a water-jet pump.

A colorless transparent syrup is obtained, giving an acidic reaction. After some time the syrup darkened and acquired a sharp odor. The product exploded when introduced into the flame of a burner.

2. Preparation of O-glycosides. To a solution of 0.005 g of acetohalogenose in 15 ml of the corresponding alcohol containing 2 g of powdered calcium carbonate, with stirring by a magnetic stirrer, a solution of 0.005 g of silver perchlorate in 10–15 ml of the same alcohol is added dropwise over 15–20 min. The precipitate is filtered off; the filtrate is evaporated in vacuo with a water-jet pump at room temperature or with gentle heating on a water bath. The residue is triturated with water, then filtered off and recrystallized from ethanol. The identity of the product is determined by thin-layer chromatography on aluminum oxide (solvent chloroform—methanol 2 : 3). For the substances obtained, Fehling' s test was carried out and gave a negative result in all cases.

For a series of alcohols (see Table 1) the reaction was carried out in acetone using a fourfold excess of alcohol.

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Note: Figure translations are in progress. See original paper for figures.