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ACIDIC DEACETYLATION OF SUGAR ACETATES

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A RECENT communication[1] on the catalytic deacetylation of per-O-acetyl-glycopyranosylbenzenes in methanolic solution in the presence of small amounts of perchloric acid, prompts us to summarize our results with the catalytic acidic deacetylation of per-O-acetyl derivatives of sugars and their derivatives.

The alkaline Zemplén's deacetylation is a very well known method and some difficulties may occur only with per-O-acetylated derivatives of reducing sugars. There are not many papers describing the acidic deacetylation,[2-4] however, only the last paper[4] describes a procedure similar to that of ours and giving bad yields. A systematic study has not yet been undertaken.

Methanolic hydrogen chloride is an unsuitable reagent, as per-O-acetylated derivatives of reducing sugars are converted mostly

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[1] Yu.A. Zhdanov, G.A. Korol'chenko, and G.N. Dorofeenko, Dokl. Akad. Nauk S.S.S.R. 143, 852 (1962).

[2] M. Zief and R.C. Hockett, J. Amer. Chem. Soc. 67, 1267 (1945).

[3] H. Lichti and A. Wartburg, Helv. Chim. acta 44, 238 (1961).

[4] J. Fernandez-Bolanos, R. Guzman de Fernandez-Bolanos, An. real.Soc. esp. Fis. Quim. 53 B, 377 (1957); Chem.Abstr. 54, 24410 (1960).

into a mixture of a free sugar and its methyl glycosides. However, methanol with several drops of concentrated hydrochloric acid gives good results in many cases. The following procedure has been used generally : 1C g of the per-O-acetylated substance has been suspended in 10 ml MeOH containing 5 drops of concentrated hydrochloric acid. After standing for 24 hours at room temperature, the crystals separated were filtered off and recrystalized. Some more substance can be obtained by standing for a longer period (3-5 days), especially in a refrigerator.

The course of the deacetylation and the purity of the products obtained has been followed using paper chromatography (Whatman No 1, n-butanol-acetic acid-water 4 : 1 : 5, descending, detection after Bonner[5]).

Under these conditions, a formation of anhydro derivatives has never been observed and D-mannitol was obtained from its hexa-O-acetyl derivative in a 95% yield. The following sugars were obtained from their per-O-acetylated derivatives: D-glucose (yield 74%), D-galactose (88%), D-mannose (40%), D-arabinose (66%), lactose (83%) and cellobiose (88%). Mother liquors contained generally some methyl glycosides and sometimes reversion products. Not a trace of saccharose has been formed under a variety of conditions from its octa-O-acetylderivative and only products of hydrolysis were observed.

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[5] T.G. Bonner, Chem. & Ind. (Rev.) (London), 345 (1960).

The following sugar derivatives have been obtained similarly from their per-O-acetyl derivatives: methyl α-D-glucopyranoside (82%), methyl β-D-glucopyranoside (75%), phenyl α-D-glucopyranoside (67%), phenyl α-cellobioside (56%), phenyl β-cellobioside (43%) and others. This method is especially useful for the deacetylation of halogendeoxy derivatives, later of mesyl- and tosyl-esters, which may give anhydroderivatives under the condition of Zemplen's deacetylation, later for the deacetylation of per-O-acetylderivatives of glycopyranosyl mercaptans, which may undergo oxidation easily. Details will be published elsewhere.