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Abstract

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CATALYTIC DEACETYLATION BY PERCHLORIC ACID IN A SERIES OF CARBOHYDRATES

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Carbohydrates and their diverse derivatives containing a polyhydric-alcohol chain are often isolated from reaction mixtures and purified through their acetates. To obtain the free products subsequently, various deacetylation methods are used, with sodium methylate, ammonia, sulfuric acid, boron trifluoride, etc. However, these methods do not always give good results. Thus, the carbohydrate derivatives of carbohydrates studied by us, usually isolated in the form of acetates, are obtained in the free state by the action of ammonia on a methanolic solution of the acetate. As a result, a large amount of absolute methanol is consumed, and the product contains a considerable quantity of acetamide, which is difficult to remove. This makes it necessary to seek new methods for deacetylating carbohydrate derivatives.

One such method proved to be catalytic deacetylation in the presence of perchloric acid. The method we propose consists in boiling a methanolic solution of a carbohydrate acetate with several drops of 60% perchloric acid. In this way we have isolated from their acetates *D*-glucopyranosylbenzene, *D*-galactopyranosylbenzene, *D*-xylopyranosylbenzene, *D*-glucopyranosyldiphenyl, *L*-arabopyranosylbenzene, and *D*-glucopyranosylpropene. The last three substances are described for the first time. The advantages of the method over others lie in its simplicity, the small expenditure of time, the ease of isolating the final product, and the absence of impurities that are difficult to separate. The yields of the final products are sufficiently high. We attempted to extend the method to other classes of polyhydroxy compounds. As a result, it proved possible to isolate the free alcohols from the acetates of mannitol, dulcitol, and inositol. When the tetraacetate of α-methylglucoside was boiled with perchloric acid, hydrolysis of the glucosidic bond was not observed, and deacetylated α-methylglucoside was isolated by us. Deacetylation of the pentaacetates of glucose and galactose led to noncrystallizing syrups.

On the basis of the available data, the new deacetylation method can be recommended as a preparative one for isolating C-derivatives of carbohydrates and polyhydric alcohols from acetates.

The acetates of C-substituted carbohydrates taken as starting materials were prepared by the procedures described by us earlier ([1], [2]).

Experimental Part

D-Glucopyranosylbenzene. To a suspension of 1.6 g of 2,3,4,6-tetraacetyl-*D*-glucopyranosylbenzene in 20 ml of absolute methanol, three drops of 60% perchloric acid were added. The mixture was heated on a gently boiling water bath for two hours. After cooling, the perchloric acid was neutralized by shaking with sodium bicarbonate. The filtered solution was evaporated on a water bath until a thick syrup formed. The syrup was washed with anhydrous ether and then extracted with ethyl acetate. After distilling off the ethyl acetate and drying in a vacuum desiccator over phosphorus pentoxide,

phosphorus gave 0.78 g of a colorless, noncrystallizing product (83% of theory).

Found, %: C 59.78; H 6.91
$C_{12}H_{16}O_5$. Calculated, %: C 60.00; H 6.66

D-galactopyranosylbenzene. To a solution of 4 g of 2,3,4,6-tetraacetyl-D-galactopyranosylbenzene in 60 ml of absolute methanol, 4 drops of 60% perchloric acid were added. The mixture was heated for two hours, after which it was worked up by the method described above. This gave 1.6 g of crystalline D-galactopyranosylbenzene with m.p. 142–143°. Yield 68% of theory.

Found, %: C 59.88; H 6.75
$C_{12}H_{16}O_5$. Calculated, %: C 60.00; H 6.66

D-xylopyranosylbenzene. To a solution of 1.6 g of 2,3,4-triacetyl-D-xylopyranosylbenzene in 25 ml of absolute methanol, three drops of perchloric acid were added. The mixture was heated for 1.5–2 hours on a water bath. After neutralization and evaporation, a precipitate separated, which was washed with ether and recrystallized from ethyl acetate. This gave 0.72 g (72% of theory) of shiny needles of D-xylopyranosylbenzene with m.p. 144–145°.

Found, %: C 62.77; H 6.84
$C_{11}H_{14}O_4$. Calculated, %: C 62.85; H 6.66

L-arabopyranosylbenzene. A solution of 2 g of 2,3,4-triacetyl-L-arabopyranosylbenzene in 35 ml of absolute methanol was heated with three drops of perchloric acid for 1.5 hours. The syrup obtained after neutralization and removal of the solvent was washed with ether and extracted with ethyl acetate. On dilution of the ethyl acetate solution with ether, a syrupy precipitate separated, which did not crystallize on prolonged storage in a vacuum desiccator. This gave 1.04 g of a colorless transparent glassy substance. Yield 84% of theory. The substance is soluble in water, alcohol, and ethyl acetate, and insoluble in ether. Described for the first time.

Found, %: C 62.67; H 6.91
$C_{11}H_{14}O_4$. Calculated, %: C 62.85; H 6.66

chemical structural formula

Figure 1: chemical structural formula

structural formula

Figure 2: structural formula

D-glucopyranosyldiphenyl. A solution of 1.5 g of 2,3,4,6-tetraacetyl-D-glucopyranosyldiphenyl in 15 ml of absolute methanol was boiled for 1.5 hours with two drops of perchloric acid. Further work-up was carried out by the described procedure. D-glucopyranosyldiphenyl was isolated as a crystalline product with m.p. 156–158°. Yield 0.65 g (72% of theory). The substance is soluble in water, alcohols, and ethyl acetate, and insoluble in ether. Described for the first time.

Found, %: C 68.26; H 6.41
$C_{18}H_{20}O_5$. Calculated, %: C 68.35; H 6.32

The structure of the substance is described by the following formula:

1-D-glucopyranosylpropene-2. A solution of 2 g of 2,3,4,6-tetraacetyl-D-glucopyranosylpropene-2 was boiled for two hours with three drops of perchloric acid in absolute methanol. After the described work-up, a noncrystallizing transparent syrup was isolated from ethyl acetate. Yield of the final product 1.1 g (82.7% of theory). The substance is soluble in water and alcohols, and insoluble in ether and benzene. Described for the first time.

Found, %: C 52.71; H 8.03
$C_9H_{16}O_5$. Calculated, %: C 52.94; H 7.84

The structure of 1-*D*-glucopyranosylpropene-2 is represented by the following structural formula:

α-Methyl-*D*-glucoside. A solution of 6 g of α-methyl-*D*-glucoside tetraacetate in 60 ml of abs. methanol was boiled for two hours with five drops of 60% perchloric acid. After evaporation of two thirds of the solvent, the mixture was left in a refrigerator. The precipitate that separated was filtered off and recrystallized from ethanol. This gave 2.1 g (67% of theory) of α-methyl-*D*-glucoside with m.p. 164–166°, which corresponds to the literature data. The substance does not give Fehling' s reaction, and there is no depression of the melting point on mixing with authentic α-methyl-*D*-glucoside.

Mannitol, dulcitol, and *i*-inositol. The indicated polyhydric alcohols were obtained in an analogous manner from their complete acetates. Usually, after completion of the reaction, half of the solvent was distilled off and the reaction mixture was placed in a refrigerator. The precipitate that separated was filtered off, washed several times with ether, and recrystallized from water. Yields of pure products were, respectively: mannitol 78%, dulcitol 52%, *i*-inositol 65%.

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