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Abstract

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CATALYTIC ACETYLATION OF POLYHYDROXY COMPOUNDS IN THE PRESENCE OF MAGNESIUM PERCHLORATE

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Acetylation of polyhydroxy compounds (polyhydric alcohols, carbohydrates and their derivatives) is usually carried out by the action of acetic anhydride in the presence of the following catalysts or condensing agents: sodium acetate (^1), pyridine (^2), sulfuric acid (^3), or zinc chloride (^4). Comparatively recently, perchloric acid, which has certain advantages over other catalysts, has begun to be used as a catalyst for the acylation of polyhydric alcohols and some carbohydrates (^5). However, when perchloric acid and other acid catalysts are used—although in general they give fairly good results—in individual cases considerable resinification is observed, or the desired product is not formed at all. Earlier, one of us showed that, in the acylation of acidophobic heterocyclic and other analogous compounds, magnesium perchlorate (anhydrone), which has high catalytic activity and gives almost no resinification products, should be preferred to perchloric acid ([6,7]).

In the present work this catalyst was used for the acetylation of certain polyhydroxy compounds of the hexitol series, mono- and disaccharides, O-glycosides, and some other carbohydrate derivatives. The acetylating agent in this reaction is apparently acetyl perchlorate $[CH_3CO]^+ClO_4^-$, which, as shown earlier (^7), can be formed by the interaction of acetic anhydride and magnesium perchlorate in the presence of the substance being acylated. Acetylation of polyhydroxy compounds in the presence of small catalytic amounts of magnesium perchlorate proceeds rapidly under very mild conditions, and in a number of cases products are formed in high yield that do not require further purification. The proposed method gives especially good results in the acetylation of polyhydric alcohols and cyclitols, where the yield of polyacetates reaches 85-90%. In analogous fashion, acetylation of D-glucose gives pure α-pentaacetate in 77-80% yield.

In the acetylation of D-galactose in the presence of anhydrone, as with perchloric acid (^5), a syrup-like product is formed, from which the pentaacetate could be isolated only in low yield. However, we have not yet succeeded in finding suitable conditions for the acetylation of pentoses and other monosaccharides. Some monosaccharide derivatives are also readily acetylated in the presence of

$Mg(ClO_4)_2$. In this way, 2,3,4,5,6-tetraacetate of O-methyl-D-glucoside was obtained, and aldose oximes were converted into acetylated aldononitriles.

In the case of acetylation of disaccharides, a mixture of acylation products is formed. Octaacetate was obtained from lactose, whereas maltose and sucrose form syrup-like products from which individual substances could not be isolated. As a model synthesis, we studied the reaction described on monohydric alcohols. Under the conditions of the acylation reaction, monohydric alcohols are smoothly converted into the corresponding acetates in high yield.

Experimental Part

Hexaacetate of *D*-mannitol. Into a three-neck round-bottom flask of 250 ml capacity, equipped with a mechanical stirrer and a thermometer, are placed 100 ml of acetic anhydride and 1 g of magnesium perchlorate. To the solution thus formed, 2–3 g of *D*-mannitol is added, the stirrer is started, and the mixture is heated on a water bath to 50–55°. After all the mannitol has dissolved, the next portion is added, care being taken that the temperature of the mixture does not rise above 60°. After all the mannitol has been added (20 g over 20–25 min), the reaction mixture is stirred at the same temperature for a further 10–15 min, cooled to room temperature, and poured with vigorous stirring into 500–600 ml of water with ice. After several hours the resulting colorless precipitate is filtered off, thoroughly washed with water, and dried in air. This gives 42.2 g (88.5% of theoretical) of a colorless crystalline powder with m.p. 117–119°. After recrystallization from alcohol, 1,2,3,4,5,6-hexaacetyl-*D*-mannitol is obtained as large transparent crystals with m.p. 120–121°. According to the literature data (8), m.p. 121–122°.

Data on the reaction conditions for acylation of polyhydric alcohols, carbohydrates, and their derivatives are given in Table 1.

Table 1

Acylated substance	Reaction temp., °C	Reaction duration, min	Product obtained	Yield, % of theoretical	M.p., °C determined	M.p., °C according to literature data	Literature source
D-Sorbitol	50–55	30–35	1,2,3,4,5,6-hexaacetyl-*D*-sorbitol	63	98.5–99.5	99	(9)
Dulcitol	60–70	30–35	1,2,3,4,5,6-hexaacetyl-dulcitol	85–85	170–171	171	(10)

Acylated substance	Reaction temp., °C	Reaction duration, min	Product obtained	Yield, % of theoretical	M.p., °C determined	M.p., °C according to literature data	Literature source
i-Inositol	60–70	30–35	1,2,3,4,5,6-hexaacetyl-*i*-inositol	82	215–216	216	(11)
Pentaerythritol	Boiling	15	Tetraacetylpentaerythritol	67–70	82	82–83	(11)
D-Glucose	40–50	30–35	1,2,3,4,6-pentaacetyl-*D*-glucose	77–78	113–114[1]	114–114.5	(12)
D-Galactose	55–56	30–35	1,2,3,4,6-pentaacetyl-*D*-galactose	10	94–95[2]	99.5	(13)
α-Methyl-*D*-glucoside	45–55	30–35	2,3,4,6-tetraacetyl-α-methylglucoside	60	100–101[3]	100–101	(4)
Oxime of *L*-arabinose	Boiling	60–60	Nitrile of 2,3,4,5-tetraacetyl-*L*-arabonic acid	40–45	117–118	117–118	(11)
Oxime of *D*-galactose	Boiling	30–60	Nitrile of 2,3,4,5,6-pentaacetyl-*D*-galactonic acid	20–25	133–134	135	(14)
Oxime of *D*-mannose	Boiling	30	Nitrile of 2,3,4,5,6-pentaacetyl-*D*-mannonic acid	Low	90–92	93–94	(11)

Acylated substance	Reaction temp., °C	Reaction duration, min	Product obtained	Yield, % of theoretical	M.p., °C determined	M.p., °C according to literature data	Literature source
n-Amyl alcohol	95–100	60	*n*-Amyl acetate	67.5	148–151[4]	148 (737)	(11)
Isoamyl alcohol	95–100	60	Isoamyl acetate	35	139–142	142	(11)
n-Hexyl alcohol	95–100	60	*n*-Hexyl acetate	75	166–169	169	(11)
n-Octyl alcohol	95–100	60	*n*-Octyl acetate	82	207–210	210	(11)
n-Nonyl alcohol	95–100	60	*n*-Nonyl acetate	60	222–225	—	(11)

Note. In all experiments for the acylation of polyhydroxy compounds, 50–100 ml of acetic anhydride and 0.5–1 g of magnesium perchlorate were taken per 10–20 g of substance.

[1] $[\alpha]_D^{20}$: +101.4° ($CHCl_3$); (12) $[\alpha]_D^{20}$: +101.6° ($CHCl_3$).
[2] $[\alpha]_D^{20}$: +106.1° ($CHCl_3$); (13) $[\alpha]_D^{20}$: +106.7° ($CHCl_3$).
[3] $[\alpha]_D^{20}$: +131° ($CHCl_3$); (14) $[\alpha]_D^{20}$: +131° ($CHCl_3$).
[4] Here and below the boiling temperatures of the acetates are given.

Preparation of Acetic Esters of Monohydric Alcohols*

0.2 g-mole of a monohydric alcohol is mixed in a flask equipped with a reflux condenser with 0.2 g-mole of acetic anhydride, and 1.1 g (0.005 g-mole) of magnesium perchlorate (anhydrone) is added to the solution. The reaction mixture is heated on a boiling water bath for 1 hour, cooled, and poured into 100 ml of cold water. The organic layer is separated, neutralized with a solution of sodium bicarbonate, dried over calcium chloride, and distilled. The results for the acetylation of monohydric alcohols are given in Table 1.

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* With the participation of V. I. Karban.

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