

ACETONATION OF L-SORBOSE CATALYZED BY HETEROPOLY ACIDS

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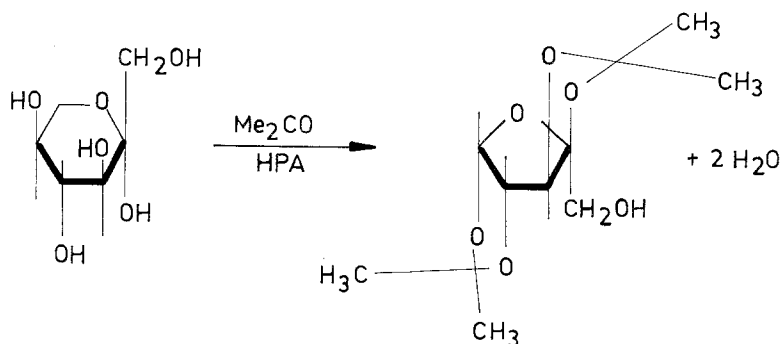
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Acetoneation of L-sorbose - a step of ascorbic acid synthesis - takes place in acetone to yield 85% of diacetone-L-sorbose in the presence of heteropoly acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ (0.1-0.35%) as catalysts.

Ацетонирование L-сорбозы - стадия синтеза L-аскорбиновой кислоты - идет в ацетоне с выходом диацетон-L-сорбозы 85% в присутствии 0.1-0.35% гетерополикислот $H_3PW_{12}O_{40}$ и $H_4SiW_{12}O_{40}$ в качестве катализаторов.

Heteropoly acids (HPA) have been extensively used as catalysts in organic synthesis [1, 2]. Of particular interest is their application in synthesizing fine chemicals, e.g. vitamins [3]. The aim of the present study was to examine tungsten HPA $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ as catalysts in acetoneation of L-sorbose to yield diacetone-L-sorbose (DAS), 2,3:4,6-di-O-isopropylidene- α -L-sorbofuranose, that is a step in producing L-ascorbic acid (vitamin C) [4].



EXPERIMENTAL

Materials

$H_3PW_{12}O_{40} \cdot nH_2O$, $H_4SiW_{12}O_{40} \cdot nH_2O$ of chemical grade and sorbose were recrystallized from water. Chemical grade acetone was used without further purification.

Acetonation

Method A. The reaction was carried out in the Soxhlet apparatus. The extractor was charged with 100 g of calcined zeolite NaA. The reaction vessel was charged with 150 ml of acetone, 0.15 g (0.047 mmol) of $H_4SiW_{12}O_{40} \cdot 18H_2O$ and 10 g (55 mmol) of sorbose. The mixture was heated to reflux under stirring for 4 h. During the reaction sorbose was dissolved and the product water was adsorbed by zeolite. The mixture was cooled to $-20^\circ C$ and kept for 0.5 h. Then it was neutralized by 10% NaOH to pH ~ 8 and cooled to room temperature. Precipitated Na salt of HPA was filtered out and acetone was distilled. The residue was mixed with 50 mol of water and then 30 mol of H_2O with mesityl oxide were distilled under vacuum. DAS was extracted from an aqueous solution by chloroform (2x50 ml). The extract was evaporated to yield 11.2 g of DAS (78%):mp $77^\circ C$ (toluene). The product was identified by TLC (Silufol UV-254 plates and acetone/hexane=3/2 eluent) using authentic samples of DAS and monoacetone-L-sorbose (MAS, 1,2-O-isopropylidene- α -L-sorbopyranose). The isolated product contained no MAS.

Method B. The reaction was carried out in a three-necked flask equipped with stirrer, dropping funnel, Liebig condenser and a collector. The reaction vessel was charged with 150 ml of acetone, 0.20 g (0.062 mmol) of $H_3PW_{12}O_{40} \cdot 18H_2O$ and 10 g (55 mmol) of sorbose. The mixture was heated to boiling and kept for 4 h. During the reaction aqueous acetone was distilled, dry acetone being continuously added from the dropping funnel to keep a constant level in the reaction vessel. Further procedure was the same as in method A. The yield of DAS was 80%.

RESULTS AND DISCUSSION

Acetonation of L-sorbose in industry is carried out in the presence of oleum to afford DAS in a 80% yield [4]. Since oleum is a catalyst and a desiccant, it is added in large excess (~5% based on acetone). The disadvantage of this method is a large quantity of waste Na_2SO_4 obtained after oleum neutralization.

Table 1
Acetonation of sorbose catalyzed by HPA in Me_2CO
([Sorbose]₀=0.37 mol/l, reflux, 4 h)

HPA	[HPA] (mmol/l)	Method	Yield of DAS (mol.%)
$H_4SiW_{12}O_{40}$	0.31	A	78
$H_4SiW_{12}O_{40}$	0.42	A	79
$H_3PW_{12}O_{40}$	0.42	A	82
$H_3PW_{12}O_{40}$	0.93	A	85
$H_4SiW_{12}O_{40}$	0.31	B	81
$H_3PW_{12}O_{40}$	0.31	B	79

In the presence of HPA the process proceeds smoothly at [HPA]=0.1-0.35 wt.% and yields up to 85% DAS (Table 1). The water formed is absorbed by NaA zeolite or removed by distillation (methods A and B). Both methods give the same yields of DAS.

Thus the application of HPA permits to increase the yield of DAS, the concentration of H^+ in the reaction system being lower by a factor of 200-700 as compared to oleum. The latter practically eliminates wastes in catalyst neutralization. After the reaction HPA can be recovered as a Na salt and then converted into HPA using conventional methods, e.g., electro-dialysis [5], and re-used.

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