

Hydration of Monoterpenic Hydrocarbons Catalyzed by Heteropoly Acids

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We have studied hydration of α -pinene (1), camphene (2) and tricyclene (3) under the utilization of heteropoly acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ (HPA P and HPA Si) as a catalyst. The influence of temperature of the process, its duration, the nature of a solvent, the quantity of a catalyst and correlation between reagents on proceeding of reaction of hydration is researched.

In a medium of dioxan α -terpineol is the main product of hydration (1). Reaction catalyzed by HPA P under temperature 65°C during three hours goes with 90% conversion and 49% yield of α -terpineol. Together with hydration, isomerization (1) proceeds, and camphene, dipentene, terpinolene etc. are produced as a result of it.

Under hydration (2) and (3) with selectivity 97-99% isoborneol is produced. The yield of isoborneol is, correspondingly, 49.5 and 37.0%. Hydration (2) in dioxan is turnabout equilibrium reaction of pseudo-primary order with equilibrium constant which is equal to 1.

We have ascertained that such solvents as tetrahydrofuran, acetone, methylethylketone, acetonitrile have not essentially influence on conversion, selectivity, yield and compound of products of reaction. In hydroalcoholic mediums, together with isoborneol, corresponding simple isobornyl ethers appear in products of hydration (2). Correlation between resultants of reaction and rate of their accumulation depends on the nature of alcohol. So, under temperature 65°C in three hours, correlation between ether and isoborneol in products of hydration of camphene in methyl, ethyl and isopropyl alcohols catalyzed HPA Si became, correspondingly: 83% and 9%, 50% and 28%, 19.5% and 45 %.

Interaction between camphene and methyl, ethyl and isopropyl alcohols catalyzed HPA Si and P, in lack of water, leads to producing of only corresponding simple isobornyl ethers with yield of 78-87%. It's necessary to notice that, in distinction from such acid catalyst as, for example, H_2SO_4 , utilization of HPA Si and P allowed to get tertiary-butyl isobornyl ether with yield of 52.6% else.