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Academician of the Academy of Sciences of the Kazakh SSR M. I. Goryaev, V. I. Shabalina,

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Abstract

Full Text

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ON THE QUESTION OF THE ACID ISOMERIZATION OF SABINENE

This paper presents data on the isomerization of *d*-sabinene under the action of the cation-exchange resin KU-1 and metatitanic acid. It is shown that, as a result of the acid isomerization of *d*-sabinene, the final products are not only α- and γ-terpinenes ([1–4]), but also terpinolene.

The bicyclic hydrocarbon sabinene (I) is readily isomerized under the influence of acid catalysts. Studies ([1–4]) devoted to this process have shown that the principal components of the acid isomerization are α- and γ-terpinenes (II, III). In addition to these substances, Δ^3-menthene and *p*-cymene have been detected in the isomerization products. It is assumed that the latter products are formed by partial disproportionation of sabinene under the influence of acid agents

$$\text{(I)} \longrightarrow \text{(IV)} + \text{(V)}$$

Moreover, it is believed that *p*-cymene may be formed as a result of oxidation of γ-terpinene

$$\text{(III)} \xrightarrow{20} \text{(IV)} + \mathrm{H_2O_2}$$

The mechanism of the acid isomerization of sabinene was proposed by Verghese ([4]), who considers that the conversion of sabinene into a mixture of α- and γ-terpinenes proceeds according to the carbonium principle:

$$\text{(I)} \xrightarrow{+\mathrm{H^+}} \text{(VI)} \xrightarrow{-\mathrm{H^+}} \text{(III)} + \text{(II)}$$

If one proceeds from this scheme, then it is natural to expect in the products of acid isomerization, in addition to α- and γ-terpinenes (II and III), one more hydrocarbon—terpinolene, since, apparently, the intermediate ion—the carbonium ion (VI)—can equally well split off a proton with formation of a double bond between the ring and the isopropyl group:

$$\text{(VI)} \xrightarrow{-\text{H}^+} \text{(VII)}$$

To clarify this question, we carried out the isomerization of sabinene using metatitanic acid and the cation-exchange resin KU-1, which acts on terpene hydrocarbons similarly to other acid catalysts. Highly active *d*-sabinene was used in the work, having the following constants: n_D^{20} 1.4668; $[\alpha]_D^{20} + 106^\circ$; d_4^{20} 0.8480.

d-Sabinene with 0.5% catalyst, under constant stirring with a stirrer, was heated at 120–140° until the optical activity of the mixture disappeared.

For analysis of the isomerizates obtained, the method of gas-liquid chromatography was used. The main components were isolated by preparative gas-liquid chromatography (Fig. 1). The components isolated in the pure state (99.5–99.7% purity) were identified with the aid of infrared spectra, as well as by obtaining characteristic crystalline derivatives. For gas-liquid chromatography, a UKh-1 instrument was used; column length 210 cm, diameter 0.4 cm, solid support INZ-600 with particle size 0.25–0.50 mm, stationary phase–anhydrous lanolin (15%), carrier gas H_2, 90 ml/min. It is seen from it that the isomerizates consist of six components, two of which are present as traces. These are unreacted sabinene and Δ^3-menthene (peaks 1 and 2). The quantitative composition of the isomerizates, determined by cutting out and weighing the paper strip under the peaks, as well as by measuring their areas, is given in Table 1.

Fig. 1. Gas-liquid chromatogram of the products of isomerization of *d*-sabinene under the action of KU-1 (*I*) and metatitanic acid (*II*). 1 –*d*-sabinene, 2 –Δ^3-menthene, 3 –α-terpinene, 4 –*n*-cymene, 5 –γ-terpinene, 6 –terpinolene

Table 1

Catalyst	*d*-sabinene	Δ^3-menthene	α-terpinene	*n*-cymene	γ-terpinene	terpinolene
1. KU-1	1	1.5	40	15	23.5	19
2. Metatitanic acid	1.5	1.5	25.5	4	46	21.5

Weight amount of component in the mixture (in %).

From the data of Table 1 it is seen that terpinolene is present in significant amounts (20%) in the products of isomerization of *d*-sabinene. Thus, during the acid isomerization of *d*-sabinene, three of its isomers are formed–α-terpinene, γ-terpinene, and terpinolene.

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