STUDY OF SUBSTANCES CONTAINED IN ESSENTIAL OILS

XX. Isomeric Conversions of d-Sabinene under the Influence of KU-1 Cation-Exchanger and Metatitanic Acid

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The bicyclic hydrocarbon sabinene (I) readily isomerizes under the influence of acidic reagents. Wallach [1] was the first to study the action of dilute sulfuric acid on this hydrocarbon, and he detected α-terpinene (II) and γ-terpinene (III) in the mixture obtained. Subsequently, other acids were used to investigate this reaction: oxalic [2] and metatitanic [3].

The authors of the papers mentioned consider that the main components of the acid isomerization of sabinene are α- and γ-terpinenes. A mechanism for this reaction has been proposed by Verghes [4], on the assumption that the conversion of sabinene into monocyclic hydrocarbons takes place by a carbonium mechanism. According to this assumption, the isomerisation of sabinene takes place through the migration of the exocyclic double bond into the cyclohexane ring and the rupture of the cyclopropane ring.

The present paper describes the isomeric conversions of d-sabinene under the influence of the cation-exchange resin KU-1. This cation-exchanger has some advantages as compared with other catalysts used for the isomerization of hydrocarbons: it possesses a high acidity in association with insolubility in hydrocarbons (which allows the isomerizate to be separated from the catalyst easily).

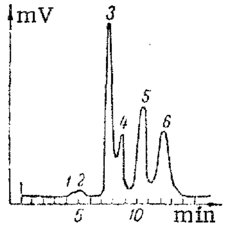
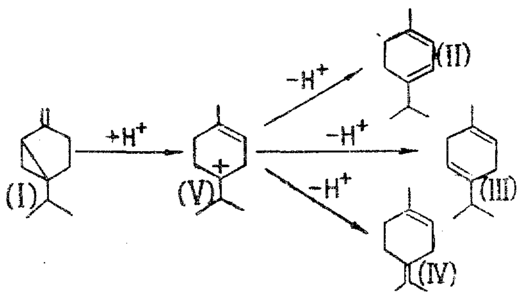


Fig. 1. Gas-liquid chromatogram of the isomerizate of d-sabinene obtained under the action of KU-1: 1) unidentified substance; 2) sabinene; 3) α-terpinene; 4) p-cymene; 5) γ-terpinene; 6) terpinolene.

The reaction was carried out by heating in the presence of 0.5 part by weight of activated KU-1, with vigorous mechanical stirring. The course of the reaction was followed by measuring the angle of rotation, which fell to zero under the given conditions. The analysis of the isomerizate was effected by gas-liquid chromatography (GLC). The main components were isolated in the pure state by the method of preparative GLC and were identified by means of their infra-red spectra and also by the preparation of characteristic crystalline derivatives.

The use of the methods of analysis mentioned for the study of the reaction permitted the acquisition of important additional information: the quantitative composition of the components of the isomerizate was determined more accurately; in addition, besides α- and γ-terpinenes and p-cymene, terpinolene (IV) was found in the reaction products. This hydrocarbon is not mentioned in earlier papers [1-4] on the acid isomerization of d-sabinene. We have assumed that the action of KU-1 on sabinene is not specific and that therefore the qualitative composition of the isomerizate obtained by the action of other acid catalysis on d-sabinene should not differ from that which we have obtained. To confirm this, we carried out the previously described [3] isomerization of sabinene in the presence of metatitanic acid. As analysis shows, terpinolene is one of the main products of the acid isomerization of d-sabinene. Thus, the mechanism of the acid isomerization of sabinene can be represented by the following scheme.



The intermediate carbonium ion (V) loses a proton in the three theoretically possible directions.

Experimental

The isomerization was carried out with highly active d-sabinene isolated from the essential oil of Juniperus sabina L. (juniper) with the constants n_D^{20} 1.4668; $[\alpha]_D^{20}$ +106°; d_4^{20} 0.8480.

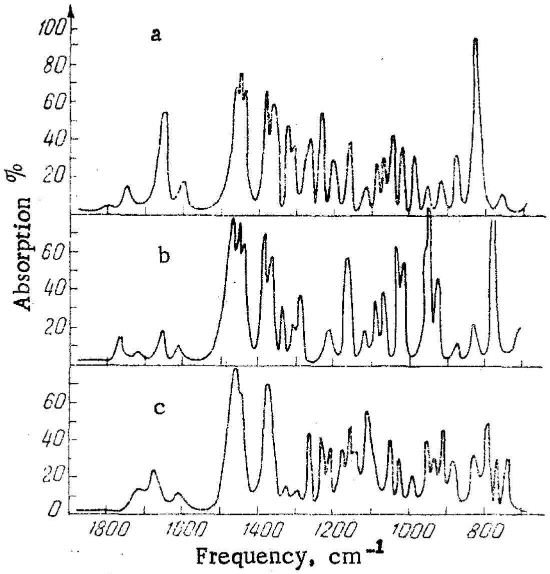


Fig. 2. IR spectra of α-terpinene (a), γ-terpinene (b), and terpinolene (c) (the spectra were obtained by means of a IKS-14 infrared spectrometer using an NaCl prism. Layer thickness 0.025 mm).

The cation-exchange resin KU-1 was treated with 5% hydrochloric acid and was washed with water and then with ethyl alcohol. The catalyst filtered off from the alcohol was dried in the air.

A mixture of 160 g of d-sabinene and 0.8 g of treated ion-exchanger was heated for 2 hr to 120° with vigorous stirring. After the reaction mixture had been cooled, the catalyst was filtered off. A small amount of the isomerizate was investigated by the GLC method on a UKh-1 gas chromatograph using a copper column 210 cm long and 4 mm in internal diameter. The carrier used was INZ-600 brick with a grain size of 0.50-0.25 mm. The stationary phase was anhydrous lanolin in an amount of 15% of the weight of the solid carrier.

The carrier gas was hydrogen at the rate of 90 ml/min, the pressure at the column inlet being 2 atm and at the outlet 1.4 atm. The column temperature was 120°. The chromatogram of the isomerizate is shown in Fig. 1. It can be seen from this that the mixture consists of six components, two of which are present only as traces. To identify the components, the isomerizate was subjected to vacuum distillation, giving a series of fractions of which those having similar refractive indices were combined to give four final fractions. Chromatography showed that the distribution of the components of the isomerizate on the lanolin took place in accordance with their boiling points. Thus, the first fraction was found to contain the components corresponding to the first two peaks of the chromatogram; the second fraction contained mainly the component corresponding to the third peak; and the fourth fraction contained a mixture of components corresponding to the third, fourth, and fifth peaks in equal amounts. The fourth fraction consisted mainly of the component corresponding to the fifth peak. Finally, the still residue contained three substances corresponding to the fourth, fifth, and sixth peaks on the chromatogram.

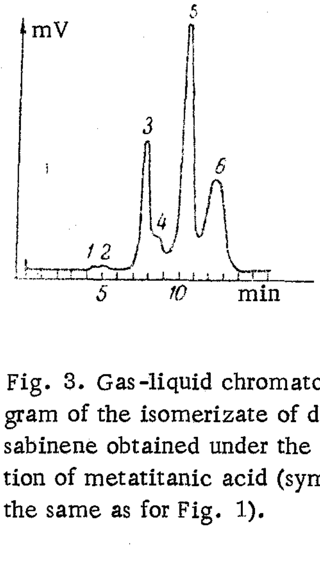


Fig. 3. Gas-liquid chromatogram of the isomerizate of d-sabinene obtained under the action of metatitanic acid (symbols the same as for Fig. 1).

From the fractions, by preparative GLC, the substances corresponding to the third, fifth, and sixth peaks were isolated in the pure state.

The isolation was carried out on the same chromatograph using a brass tube 270 cm long with an internal diameter of 9 mm. The carrier gas was hydrogen and the solid carrier was INZ-600 brick with a grain size of 0.50-0.25 mm. The stationary liquid phase was lanolin in an amount of 30% of the weight of the solid carrier.

The rate of flow of gas was 150 ml/min. The column temperature was 140°, and the detector bridge current was a minimum (120-140 ma).

The sample (0.15-0.20 ml) was introduced by a microsyringe. The separated material was condensed in a U-shaped glass trap having a bulb at the bend. The trap was cooled with a mixture of snow and salt. A check on the analytical column showed that the products isolated contained not more than 0.5% of impurities.

The component corresponding to the third peak had n_D^{20} 1.4784, which is close to the refractive index of α-terpinene. For identification, we prepared the adduct with maleic anhydride by G. A. Rudakov and M. M. Shestaeva's method [5], and then converted the adduct into the corresponding dicarboxylic acid (mp 147-148°).

The IR spectrum of α-terpinene (Fig. 2, a) differs somewhat from the spectrum of α-terpinene given in a paper by G. V. Pigulevskii and A. T. Ryskal'chuk [6]. The component corresponding to the fifth peak had an IR spectrum (Fig. 2, b) identical with that of γ-terpinene [7]. Chemically, the γ-terpinene was converted into the nitrosate, the melting point of which (116-118°) corresponded to that given in the literature [8]. The IR spectrum of the component corresponding to the sixth peak is shown in Fig. 2, c. It is identical with the spectrum of terpinolene [7]. Its identification as terpinolene was again confirmed by the preparation of the nitrosite with mp 155°.

The IR spectra of the second and third fractions of the isomerizate contained a fairly strong line in the 1510 cm^{-1} region. Since this line is not shown by α- and γ-terpinenes, it is natural to assume that it corresponds to the component of the fourth peak and relates to the vibrations of the benzene ring in p-cymene. In actual fact, when p-cymene was added to the isomerizate the fourth peak became larger. A similar increase in the size of the second peak took place when d-sabinene was added. Thus, the isomerization of d-sabinene under the action of KU-1 forms a mixture consisting of 40% of α-terpinene, 23.5% of γ-terpinene, 19% of terpinolene, 15% of p-cymene, 1% of sabinene, and 1.5% of an unidentified substance.

Isomerization of d-sabinene under the influence of metatitanic acid. A mixture of 15 g of d-sabinene and 0.15 g of metatitanic acid was heated at 140° with mechanical stirring until the optical activity had disappeared (3 hr). The chromatogram of the resulting isomerizate is shown in Fig. 3. The isomerizate consisted of 25.5% of α-terpinene, 46% of γ-terpinene, 21.5% of terpinolene, and 4% of p-cymene. The unchanged sabinene and the unknown substance amounted to 3%.

Summary

1. The action of KU-1 cation exchange resin on d-sabinene has been studied. This cation-exchanger causes the isomerization of d-sabinene, like other acidic catalysts.

2. In the acid isomerization of d-sabinene, in addition to α- and γ-terpinenes and p-cymene, which had been found previously, terpinolene is formed.

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