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Abstract

Full Text

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ON THE REDUCTION OF Δ^3-CARENE OXIDE

In the communication on the reduction of the oxides of α-pinene and Δ^3-carene (^{1}), only a few preliminary data were given on the nature of the products of the reduction reaction of Δ^3-carene oxide in the presence of Raney nickel. It was shown that under these conditions Δ^3-carene oxide is reduced to an alcohol of composition $C_{10}H_{18}O$, giving crystalline derivatives: 3,5-dinitrobenzoate (m.p. 131–132°) and the acid phthalate (m.p. 158–159°).

Upon a more detailed study of the hydrogenation reaction of Δ^3-carene oxide over Raney nickel, we found that, in addition to the above-mentioned product, two further products are formed—alcohols with the same general formula $C_{10}H_{18}O$.

As was already indicated, the first alcohol is apparently identical with *l*-caranol-3, obtained by Kuchinskii and Khabudzinskii (^{2}) by the action of powdered sodium in benzene on Δ^3-carene oxide and by the reduction with sodium in ethanol of the isomerization product of Δ^3-carene oxide, *l*-caranone-3.

The alcohol from the reduction reaction of *l*-caranone-3, subjected by the authors to double purification through the *p*-nitrobenzoate and the acid phthalate, has constants very close to those of the alcohol obtained by us and purified through the 3,5-dinitrobenzoate.

Literature data: b.p. 110°/20 mm, d_4^{20} 0.9516, n_D^{20} 1.4808, $[\alpha]_D = -67.1°$, acid phthalate, m.p. 151.5° (^{2}); b.p. 106.5–107°/13 mm, d_4^{20} 0.9520, n_D^{20} 1.4822, $[\alpha]_D = -70.05°$, acid phthalate, m.p. 158–159° (^{1}). Thus, the alcohols differ somewhat only in the melting point of the acid phthalate: we obtained a crystalline derivative with a higher melting point.

On oxidation of the product of hydrogenation of Δ^3-carene oxide over Raney nickel with chromic anhydride in acetic acid, a ketone $C_{10}H_{16}O$ was obtained, giving, in quantitative yield, a semicarbazone with m.p. 201–202°.

According to the constants and the melting point of the semicarbazone, the ketone is identical with *l*-caranone-3 (^{2})—the product of isomerization of Δ^3-carene oxide by sodium in benzene. Constants of the ketone purified by us through the semicarbazone: b.p. 81–83°/7.5 mm, n_D^{20} 1.4705, d_4^{20} 0.9467, $[\alpha]_D = -110.6°$. Constants of *l*-caranone-3 (^{2}): b.p. 98–99°/19 mm, n_D^{20} 1.4703, d_4^{20} 0.9507, $[\alpha]_D = -140°$. The same ketone was obtained by us in low yield in the dehydration reaction of β-careneglycol with p-toluenesulfonyl chloride in pyridine, the study of which had been undertaken several years ago in order to determine the direction of the reaction (I or II).

For the definitive identification of the described product of hydrogenation of Δ^3-carene oxide over Raney nickel with *l*-caranol-3, the latter was obtained by us through the action of sodium on Δ^3-carene oxide in benzene. In doing so, we also pursued another objective: the preparation of the sodium-isomerization product of the oxide, *l*-caranone-3, and the study of its reduction reaction with $LiAlH_4$.

From the alcoholic fractions there were obtained the 3,5-dinitrobenzoate of *l*-caranol-3.

with m.p. 131-132° (from alcohol) and the acid phthalic ester, m.p. 158-159°, which did not depress the melting point of mixed samples with the corresponding derivatives of the product of hydrogenation of Δ^3-carene oxide over Ni-Raney. Consequently, one of the products of catalytic hydrogenation of Δ^3-carene oxide is *l*-caranol-3.

Among the products of the hydrogenation reaction we also found, in small amounts, another alcohol, $C_{10}H_{18}O$, giving a 3,5-dinitrobenzoate with m.p. 126-127° and a p-nitrobenzoate, m.p. 109-110°. From the melting point of the p-nitrobenzoate the alcohol proved to be identical with caranol-4, formed by the action of sodium on Δ^3-carene oxide in benzene and first isolated by Polish authors ([2]). According to their data, caranol-4 does not give an acid phthalic ester. We also were unable to obtain it.

It would seem that caranol-4 could easily have been isolated from the products of catalytic hydrogenation of Δ^3-carene oxide by treating them with phthalic anhydride. However, this alcohol was not isolated by us in this way, probably because of its dehydration by phthalic anhydride, as may be indicated by the formation in this reaction of small amounts of phthalic acid. The crystalline products proved to be a mixture of derivatives of two alcohols. The acid phthalic ester of *l*-caranol-3 was isolated, m.p. 158-159° (86%), and an acid phthalic ester with m.p. 102-103.5°, $[\alpha]_D = -38.96°$ (c 1.36, benzene) (14%), corresponding by analysis to the alcohol $C_{10}H_{18}O$. The latter could not be isolated in pure form by saponification of the ester because of its small amount.

The alcohol may be one of the four possible stereoisomers of caranol-3. Naturally, one would expect two of them to be formed on reduction of *l*-caranone-3 with $LiAlH_4$, since according to the literature ([3,4]), cyclic ketones under the action of $LiAlH_4$ give mixtures of stereoisomeric alcohols with predominance of the thermodynamically more stable isomers. The experiment showed that *l*-caranone-3 under the conditions of this reaction forms a mixture of two stereoisomeric alcohols, consisting of 75% of the already known *l*-caranol-3 and 25% of an alcohol with constants: b.p. 67.5-68°/3 mm, n_D^{20} 1.4826, d_4^{20} 0.9567, $[\alpha]_D = +43.57°$ (c 3.2, ethanol); MR_{found} 45.93; $C_{10}H_{18}O$, 3-membered ring MR_{calc} 46.20. The alcohol gives a 3,5-dinitrobenzoate, m.p. 103-104°, and an

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acid phthalic ester, m.p. 114-115°, $[\alpha]_D = +40.46°$ (c 1.73, benzene). Oxidation of the alcohol with chromic anhydride in acetic acid gave the starting *l*-caranone-3, semicarbazone m.p. 201-202°.

In connection with the foregoing, it seemed of interest to us to study the reduction of Δ^3-carene oxide with $LiAlH_4$.

According to literature data on the preferential cleavage of the oxide ring at the less substituted carbon atom ($^{5-8}$), in the reaction of reduction of Δ^3-carene oxide with $LiAlH_4$ one should have expected formation, as the main reaction product, of stereoisomeric tertiary alcohols. We found that the sole product of the reaction is the caranol-4 described by the Polish authors (^{2}), b.p. 76-77°/7 mm, m.p. 30-33°, $[\alpha]_D = +21.1°$ (c 2.8, ethanol); yield 65.9%; m.p. of the 3,5-dinitrobenzoate 126-127° (from benzine, b.p. 66-70°), m.p. of the *p*-nitrobenzoate 109-110°. Both esters melted without depression of the melting point when mixed with the corresponding derivatives of caranol-4 isolated from the products of catalytic hydrogenation of Δ^3-carene oxide.

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