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reaction scheme showing formation of compounds (I) and (II)

Figure 2: reaction scheme showing formation of compounds (I) and (II)

Abstract

Full Text

Chemistry

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On the Interaction of Δ^3-Carene Oxide with Methyl Alcohol in the Presence of Sodium Methylate

(Presented by Academician B. A. Arbuzov, 22 V 1963)

In the works of A. A. Petrov et al. (^{1}, ^{2}) it was shown that the order of addition of alcohols to unsymmetrical oxides depends on the nature of the catalyst. Thus, under the action of alcoholates, the oxides of isobutylene and propylene with alcohols give primary glycol ethers, i.e., the normal addition products (according to Krasuskii' s rule (^{3})). In the presence of catalysts of acidic character, alcohols add to oxides with the formation of mixtures of both possible isomers, the greater part of which consists of tertiary and, correspondingly, secondary glycol ethers.

Fig. 1. Fractionation of the reaction products of Δ^3-carene oxide with methyl alcohol in the presence of sodium methylate

In studying the reactions of bicyclic terpene oxides with alcohols, we found (^{4}, ^{5}) that Δ^3-carene oxide with methyl alcohol in the presence of sulfuric acid gives chiefly the anomalous addition product.

4-Methoxycaranol-3 (I)

and a small amount of the second addition product, which we assumed to be isomeric 3-methoxycaranol-4 (II). The low yield of the latter under acid-catalyzed reaction conditions did not allow it to be obtained in analytically pure form or its structure to be proven. In this connection, it was of interest to study the action of methyl alcohol on Δ^3-carene oxide in the presence of sodium methylate, since, according to the literature data cited by us, it should be expected that the main product of this reaction would be 3-methoxycaranol-4.

The reaction of Δ^3-carene oxide with methyl alcohol and sodium methylate as catalyst was carried out by heating the reaction mixture for 6 hours at 130–155° in sealed tubes. The reaction products were fractionated on a column with an efficiency of 17 theoretical plates. The results of the distillation are presented in Fig. 1. Five zones can be distinguished on the graph. Fractions of zone A (10.5% by weight of the reaction products) consist mainly of Δ^3-carene oxide: on hydration with 1% H_2SO_4, β-carene glycol was obtained from them. Fractions of zone B (17.8%) contain products of isomerization of Δ^3-carene oxide. Titration with perphthalic acid according to Böme (6) showed that the products of these fractions are unsaturated; moreover, the number of double bonds found for individual fractions of zone B ranges from 1.3 to 1.6, which may indicate the presence in the mixture of compounds of different degrees of unsaturation (with one and two double bonds in the molecule). According to the IR spectra (Figs. 2 and 3), the fractions of zone B contain unsaturated alcohols: in the IR spectra there are bands corresponding to $\nu_{C=C}$ (1635–1641 cm^{-1}), δC—H at C atoms connected by a double bond (834–953 cm^{-1}), νC—O of the bond between carbon and the oxygen atom of the hydroxyl group (1062 cm^{-1}), and δC—H of methyl groups not located on the cyclopropane ring (doublet 1374–1398 cm^{-1}) (7). However, the products of the fractions of zone B did not give crystalline derivatives of alcohols. Chromatographic–

Fig. 2. IR spectrum of fraction No. 13

Fig. 3. IR spectrum of fraction No. 14

It was not possible to isolate individual compounds by chromatographing the levorotatory fractions of this zone (Nos. 10–15) on aluminum oxide.

On the basis of elemental-analysis data it may be concluded that zone C (24.5%) combines fractions that are mixtures of products of isomerization of the oxide and of the product of addition of methyl alcohol to Δ^3-carene oxide, whereas the fractions of zone D (19.2%) and ε (27.5%) contain only the addition product.

However, upon treatment with 3,5-dinitrobenzoyl chloride in pyridine, some fractions of zone D (b.p. 88.5°/4 mm, n_D^{20} 1.4781, d_4^{20} 0.9888, $\alpha_D = +78.7°$) gave, in small amounts, the 3,5-dinitrobenzoate of caren-4(7)-ol-3 (8,9), m.p. 105–106°; these same fractions also gave the n-nitrobenzoate of caren-4(7)-ol-3 with m.p. 151–152°. The formation of caren-4(7)-ol-3 in this reaction is readily explicable. It is known that under the action of bases α-oxides isomerize into α,β-unsaturated alcohols (10,12). Under the conditions of the present reaction, Δ^3-carene oxide is isomerized under the influence of sodium methylate:

methylate-induced isomerization of Δ^3-carene oxide $\longrightarrow$ caren-4(7)-olate $\longrightarrow$ caren-4(7)-ol-3.

Zone ε consists of the product of addition of methyl alcohol to Δ^3-carene oxide. Esterification of the addition product with an insufficient amount of boric acid showed that it is homogeneous: the constants of the product of saponification of the boric-acid ester (b.p. 85-86°/2 mm, n_D^{20} 1.4749, d_4^{20} 0.9903, $\alpha_D = +97.7^\circ$, MR found 52.30; $C_{11}H_{20}O_2$, three-membered ring, MR calculated 52.47) and of the product that had not reacted with boric acid (b.p. 84-86°/2 mm, n_D^{20} 1.4750, d_4^{20} 0.9897, $\alpha_D = +102.2^\circ$, MR found 52.34; $C_{11}H_{20}O_2$, three-membered ring, MR calculated 52.47) proved to be identical. Both products gave a 3,5-dinitrobenzoate with m.p. 130-131°, $[\alpha]_D = +104.1^\circ$ (c 4.9, benzene).

Found, %:	C 56.97; H 6.06
$C_{11}H_{20}O_2$. Calculated, %:	C 57.14; H 5.85

It has already been noted previously that, in the reaction of Δ^3-carene oxide with methyl alcohol in the presence of base, the normal addition product, 3-methoxycaranol-4, should be formed. This structure of the addition product formed in the reaction catalyzed by sodium methylate is confirmed by data from the study of its oxidation with chromic anhydride. Upon oxidation with chromic anhydride the addition product gave a substance of composition $C_{11}H_{18}O_3$ with b.p. 99-101°/2.5 mm, n_D^{20} 1.4585, d_4^{20} 1.0154, $\alpha_D = -13^\circ$, MR found 53.26; $C_{11}H_{18}O_3$, three-membered ring, MR calculated 53.16; semicarbazone, m.p. 117-118°.

Found, %:	C 56.39; H 8.40
$C_{12}H_{21}N_3O_3$. Calculated, %:	C 56.45; H 8.29

The IR spectrum of the oxidation product has a broad band with frequency 1710-1740 cm^{-1}, which apparently is the result of the superposition of two bands with frequencies corresponding to $\nu C = O$ of ketone and ester groups. In its properties the oxidation product is close to keto ester III, described by Zemmler (^{13}). However, the melting point of the semicarbazone of keto ester III (108-110°) is somewhat lower than that of the semicarbazone of the oxidation product. The oxidation product was saponified with an alcoholic solution of caustic potash in order to obtain keto acid IV, for which the following is characteristic:

$$\text{(II) 3-methoxycaranol-4} \xrightarrow{\text{CrO}_3} \text{(III) keto ester} \longrightarrow \text{(IV) keto acid.}$$

semicarbazone with m.p. 182-183° (13). The substance obtained by saponification of the product with b.p. 99-101°/2.5 mm gave a semicarbazone, m.p. 181-182°. Keto acid IV and keto ester III can be obtained in this series of transformations if the product of the addition of methyl alcohol to Δ^3-carene oxide has the structure of 3-methoxycaranol-4 (II). Its isomer, 4-methoxycaranol-3 (I), under the action of chromic anhydride is converted into 4-methoxycaranone-3 (7).

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