Chemistry

1963

SovietRxiv

Abstract

Full Text

Chemistry

Z. G. Isaeva, I. S. Andreeva

On the Isomerization of Δ^3-Carene Oxide in Reaction with Alcohols in the Presence of Acids

(Presented by Academician B. A. Arbuzov on 3 V 1963)

In 1949 we (^{1}) found that Δ^3-carene oxide, in reaction with primary alcohols in the presence of sulfuric acid, forms products of addition of the alcohol to the oxide—tertiary monoalkyl ethers of careneglycol; under the action of secondary alcohols, along with the reaction of addition of the alcohol to the oxide, isomerization of the oxide into a carbonyl compound is also observed—an "unsaturated aldehyde of undetermined structure" ; in the case of reaction with a tertiary alcohol, only isomerization of the oxide into an aldehyde takes place.

Later Kuchinskii and co-workers found that, under the action of sulfuric acid in tert-butyl alcohol (^{2}) and acetic acid (^{3}), Δ^3-carene oxide gives a mixture of reaction products consisting of hydrocarbons (mainly *p*-cymene), *l*-caranone-3, an unsaturated monocyclic ketone, and β-careneglycol (or its monoacetate in the case of reaction with acetic acid); the "unsaturated aldehyde" was not found among the reaction products. Kuchinskii and co-workers explain this discrepancy between the data on the study of the isomerization of Δ^3-carene oxide under the action of acids by assuming that the Δ^3-carene oxide used by the authors was contaminated with α-pinene oxide, which is readily isomerized into campholenic aldehyde; the presence of campholenic aldehyde in the isomerization products of Δ^3-carene oxide caused a positive reaction with fuchsine-sulfurous acid and moist silver oxide. Such an explanation seemed unlikely to us, since, first, the "impurity" of α-pinene oxide would have to be present in rather substantial quantities in order to give one of the main isomerization products; second, a semicarbazone with m.p. 216–217°, characteristic of the "unsaturated aldehyde of undetermined structure," and the semicarbazone of campholenic aldehyde (m.p. 136–139°) can hardly be called close in melting point.

In order to clarify the causes of the indicated discrepancy and to study in greater detail the reaction of isomerization of Δ^3-carene oxide under the influence of acids, we repeated our experiments on the interaction of Δ^3-carene oxide with alcohols in the presence of sulfuric acid. The mechanism of the acid-catalyzed isomerization reaction of α-oxides generally accepted at present includes, as one of the intermediate stages, the formation of a carbonium ion, which can be stabilized by several pathways: addition of the reagent anion (formation of reaction scheme

Figure 1: reaction scheme

an addition product), electrophilic rearrangement (isomerization into carbonyl compounds), and abstraction of a proton from the β-position (isomerization into α,β-unsaturated alcohols). A transformation of bicyclic terpene oxides analogous to the last of these is observed in their reaction with acetic anhydride, with the formation of acetates of α,β-unsaturated alcohols. In the products of isomerization of terpene oxides in the presence of acids, α,β-unsaturated alcohols had not previously been detected.

In addition to the results obtained earlier (^{1}), we found that, first, opening of the oxide ring of Δ^3-carene oxide in a reaction cataly-

by an acid, proceeds in both directions: the product of addition of methyl alcohol to the oxide contains, in addition to 4-methoxycaranol-3 (I) (or the tertiary monomethyl ether of carenglycol), 3-methoxycaranol-4 (II), 3,5-dinitrobenzoate, m.p. 128-129° (yields 75% and 6%, respectively); secondly, isomerization of Δ^3-carene oxide into carbonyl compounds under the action of acid takes place to a very slight extent already in the reaction with primary alcohols: in the products of the reaction with methyl alcohol, *l*-caranone-3 (^{4}) was identified (yield 4%); semicarbazone, m.p. 199-200°; 2,4-dinitrophenylhydrazone, m.p. 158-159°. 4-Methoxycaranol-3 was isolated in pure form by saponification of its 3,5-dinitrobenzoate with m.p. 112-113°; b.p. 83-84°/3 mm, n_D^{20} 1.4810, d_4^{20} 1.006, $[\alpha]_D = -2.0°$; MR found 52.04; $C_{11}H_{20}O_2$, 3-membered ring MR calculated 52.24. On oxidation with the chromic anhydride-pyridine complex, 4-methoxycaranol-3 gave 4-methoxycaranone-3 (III): b.p. 109-111°/11 mm, n_D^{20} 1.4752, d_4^{20} 1.0013, $[\alpha]_D = +36.7°$; MR found 51.19, $C_{11}H_{18}O_2$, 3-membered ring MR calculated 50.95; semicarbazone, m.p. 213-214°; 2,4-dinitrophenylhydrazone, m.p. 147-148°. The IR spectrum of 4-methoxycaranol-3 has a band at a frequency of 1713 cm^{-1}. 4-Methoxycaranone-3

proved to be unstable toward acids. In the course of hydrolysis of the semicarbazone in the presence of acids, molecules of methyl alcohol are split off from 4-methoxycaranone-3 and unsaturated ketones of composition $C_{10}H_{14}O$ are formed. According to IR spectra, the products of hydrolysis of the semicarbazone with m.p. 213-214° by a saturated solution of oxalic acid with simultaneous steam distillation contain approximately equal amounts of 4-methoxycaranone-3 and unsaturated ketones (equal intensities of the bands at 1713 cm^{-1}, corresponding to $\nu_{\mathrm{C=O}}$ of a ketone of the cyclohexane series, and 1666 cm^{-1}, characteristic of an unsaturated ketone in the molecule of which the CO group is conjugated with two double bonds). The products of hydrolysis of the semicarbazone of 4-methoxycaranone-3 in the presence of sulfuric acid consist mainly of ketones $C_{10}H_{14}O$. Their structure has not been established by us, but the data given below allow them to be assigned to the series of *p*-

and *m*-menthadienones.

In one of the experiments on the hydrolysis of the semicarbazone of 4-methoxycaranone in the presence of sulfuric acid, a product was obtained (yield 71.6%), separated into two fractions (ratio 1:2): 1) 97-112°/12 mm, n_D^{20} 1.5245, d_4^{20} 0.9787, $[\alpha]_D = -8.35°$; 2) b.p. 112-116°/12 mm, n_D^{20} 1.5365, d_4^{20} 0.9794, $[\alpha]_D = -1.7°$. According to IR spectra, both fractions, in addition to ketones, contained phenols (bands at frequencies of 1620 cm^{-1}, 1594 cm^{-1}, 1512 cm^{-1}, 810 cm^{-1}). The phenol isolated from the hydrolysis products by extraction with sodium hydroxide solution (yield 18.5%) proved to be carvacrol (^{5}): b.p. 82-84.5°/2.5 mm, n_D^{20} 1.5220, d_4^{20} 0.9767, MR found 46.84; $C_{10}H_{14}OF_3$ MR calculated 46.30; 3,5-dinitrobenzoate, m.p. 95-96°; α-naphthylurethane, m.p. 117-118°. Mixed samples with the corresponding derivatives of carvacrol* melted without depression of the melting temperature. The ketone portion of the hydrolysis products (37%), after separation of carvacrol by distillation, was divided into 2 fractions: 1) 101-112°/7 mm—1.3 g, n_D^{20} 1.5250, d_4^{20} 0.9758, $[\alpha]_D = -17.0°$; 2) b.p. 112-115°/7 mm—1.7 g, n_D^{20} 1.5383, d_4^{20} 0.9762, $[\alpha]_D = -2.0°$. Products from the first and second fractions gave two 2,4-dinitrophenylhydrazones: 1) m.p. 179-180° and 2) m.p. 145-146°. The IR spectra of the products of these fractions have bands with frequency 1670 cm^{-1}, which may be assigned to $\nu_{C=O}$ of menthadienones with a CO group conjugated with two double bonds. Upon isomerization over 10% palladized carbon (^{6}), the product with b.p. 101-112°/7 mm gave two phenols: 1) carvacrol; 3,5-dinitrobenzoate, m.p. 94-95°, and 2) 2-methyl-4-isopropylphenol; 3,5-dinitrobenzoate, m.p. 151-152°. Consequently, ketones of the *n*- and *m*-menthadienone series are present in the mixture of products of hydrolysis of 4-methoxycaranone-3 semicarbazone with sulfuric acid.

In order to determine the relative arrangement of the C=C and C=O bonds

$$(C = C - C = C - C = O) \quad \text{or} \quad C = C - C - C = C) \qquad (7)$$

$$\|$$

$$C$$

in the molecules of the unsaturated ketones, the product with b.p. 112-115°/7 mm was oxidized with alkaline hydrogen peroxide. However, no mono- or diepoxy ketones were found in the oxidation reaction products, and only carvacrol was detected.

The data obtained in studying the reaction of Δ^3-carene oxide with isopropyl and tert-butyl alcohols proved interesting. As before (^{1}), we found that, upon the action of isopropyl alcohol on Δ^3-carene oxide, a product of addition of

---

* Carvacrol was obtained by isomerization of *d*-carvone over palladized charcoal: 3,5-dinitrobenzoate, m.p. 93-94°; α-naphthylurethane, m.p. 117-118°.

the alcohol to the oxide and carbonyl compounds are formed. In addition, *n*-cymol (6%) and β-carenglycol (yield 12%), m.p. 73-74° (monohydrate) ([8]), were identified. The addition product (yield 10%), 4-iso-propoxycaranol-3, was obtained in pure form by saponification of the 3,5-dinitrobenzoate with m.p. 151-152°: b.p. 95-97.5°/2.5 mm, n_D^{20} 1.4695, d_4^{20} 0.9585, $[\alpha]_D = +6.9°$, MR found 61.65; $C_{13}H_{24}O_2$, 3-membered ring. MR calculated 61.70; 3,5-dinitrobenzoate, m.p. 153°. The carbonyl compounds proved to be a mixture of three products: 1) an aldehyde $C_{10}H_{16}O$ (yield 3%), IR spectrum, ν C=O 1725 cm^{-1}, semicarbazone, m.p. 190-191°, identical with the aldehyde from the reaction of Δ^3-carene oxide with acetic anhydride (to be described in greater detail in one of the following communications), 2) *l*-caranone-3 (yield 7%), semicarbazone, m.p. 200-201°, and 3) a ketone $C_{10}H_{16}O$ (yield 39.5%), giving the same semicarbazone* with m.p. 216-217°, which we had assigned to an unsaturated aldehyde ([1]). By hydrolysis of the semicarbazone with m.p. 219-220° (a mixed sample with the semicarbazone, m.p. 216-217°, melted without depression of the melting point), the ketone was isolated in pure form: b.p. 67-67.5°/3.5 mm, n_D^{20} 1.4719, d_4^{20} 0.9565, $[\alpha]_D = -89.6°$, IR spectrum, ν C=O 1709 cm^{-1}; MR found 44.50, $C_{10}H_{16}O$, 3-membered ring; MR calculated 44.69; semicarbazone, m.p. 219-220°; 2,4-dinitrophenylhydrazone, m.p. 136.5°. By its constants the ketone is identical with *l*-isocaranone-3; however, the melting point of its semicarbazone is somewhat higher than that reported by Kuchinsky and Khabudzinsky ([9]) for *l*-isocaranone-3 (214.5°). We synthesized *l*-isocaranone-3 by oxidation with chromic anhydride of *l*-isocaranol-3—one of the products of hydrogenation of Δ^3-carene oxide over Raney nickel ([9,10]). A mixed sample of the 2,4-dinitrophenylhydrazones of the product of isomerization of Δ^3-carene oxide and *l*-isocaranone-3 (m.p. 135-136°) melted without depression of the melting point.

Repeated investigation of the reaction of isomerization of Δ^3-carene oxide with sulfuric acid in tert-butyl alcohol gave more complete information about the course of the reaction, although somewhat differing from the data of Kuchinsky and Khabudzinsky ([2]).

We found that, in the reaction with tert-butyl alcohol, Δ^3-carene oxide forms *l*-caranone-3 (yield 27%), *l*-isocaranone-3 (yield 14%), in small amounts the ketone $C_{10}H_{16}O$, IR spectrum, $\nu C-O$ 1705 cm^{-1}, semicarbazone, m.p. 199-199.5°, not identical with the semicarbazone of *l*-caranone-3, caren-4(7)-ol-3 (11) (10%), *n*-cymene (4%), and β-careneglycol (21%). An aldehyde with semicarbazone melting point 192-193° was not detected here. Consequently, in addition to the reaction products described in the analogous work of Kuczyński and Chabudziński, we identified *l*-isocaranone-3 and caren-4(7)-ol-3, but did not find the monocyclic unsaturated ketone.

---

* The melting point of the same semicarbazone obtained for the product of isomerization of Δ^3-carene oxide with sulfuric acid in tert-butyl alcohol is 221-222° ([1]).

Thus, the product of isomerization of Δ^3-carene oxide described by us earlier proved to be a mixture of carbonyl compounds; one of the components of this mixture—*l*-isocaranone-3—forms a semicarbazone, m.p. 219–220°. The unsaturation of the isomerization product and its reactions with fuchsin-sulfurous acid and moist silver oxide were apparently due to impurities of the aldehyde characterized by a semicarbazone with m.p. 192–193° and to the presence of previously unidentified unsaturated alcohols.

Scientific Research Chemical Institute
named after A. M. Butlerov
of Kazan State University
named after V. I. Ulyanov-Lenin

Received
28 IV 1963

CITED LITERATURE

1. Z. G. Isaeva, B. A. Arbuzov, ZhOKh, **19**, 893 (1949).
2. H. Kuczyński, A. Hendrich, Roczn. Chem., **33**, 293 (1959).
3. Z. Chabudziński, H. Kuczyński, Roczn. Chem., **33**, 871 (1959).
4. H. Kuczyński, Z. Chabudziński, Roczn. Chem., **29**, 437 (1955).
5. M. Goryaev, I. Pliva, *Methods for the Study of Essential Oils*, Alma-Ata, 1962, p. 552.
6. Ch. Balant, Ch. A. Vodoz, H. Kappeler, H. Schinz, Helv. chim. acta, **34**, 722 (1951).
7. E. Weitz, A. Scheffer, Ber., **54**, 2327 (1921).
8. B. A. Arbuzov, *Studies in the Field of Isomeric Transformations of Bicyclic Terpene Hydrocarbons and Their Oxides*, Kazan, 1936, p. 182.
9. H. Kuczyński, Z. Chabudziński, Roczn. Chem., **35**, 227 (1961).
10. B. A. Arbuzov, Z. G. Isaeva, DAN, **121**, 105 (1958).
11. B. A. Arbuzov, Z. G. Isaeva, DAN, **122**, 73 (1958).

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