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1964

SovietRxiv

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Abstract

Full Text

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ON THE STRUCTURE OF ACETATES OF UNSATURATED ALCOHOLS FROM THE REACTION OF Δ^3-CARENE OXIDE WITH ACETIC ANHYDRIDE

In 1954 we found that, under the action of acetic anhydride, Δ^3-carene oxide is converted into the acetate of a dienic alcohol of composition $C_{12}H_{18}O_2$ and the diacetate of β-carenglycol (^{1}). Later it was found (^{2}) that, first, in this reaction Δ^3-carene oxide forms, in addition to acetates, carbonyl compounds, one of which, by the melting point of its semicarbazone, was identical with the "unsaturated aldehyde of undetermined structure"—the product of isomerization of the oxide by zinc bromide and magnesium bromide (^{3}); second, the acetate $C_{12}H_{18}O_2$, isolated by fractionation of the reaction mixture on a rectification column, proved to be a bicyclic acetate with one double bond in the molecule. As possible structures for the bicyclic acetate, the structures of the acetates of caren-4(7)-ol-3 and caren-4-ol-3 were proposed, but no choice between them was made. Nor was the reason for the discrepancy in the data concerning the acetate $C_{12}H_{18}O_2$ clarified.

Fig. 1. Fractionation of the products of the reaction of Δ^3-carene oxide with acetic anhydride

We continued the study of this reaction in order to establish the nature of the acetate of the unsaturated alcohol and of the products of isomerization of Δ^3-carene oxide. Repetition of the experiments with larger quantities of the oxide and the use of spectroscopy for identification of the reaction products made it possible to obtain the more complete data presented in the present work. In Fig. 1 the results of fractionation of the products of the reaction of Δ^3-carene oxide with acetic anhydride are shown graphically. The product of fractions of zone *B* (constants after secondary fractionation on a rectification column: b.p. 85°/21 mm, n_D^{20} 1.4612, d_4^{20} 0.9281; MR_D found 44.96; $C_{10}H_{16}O$, 3-membered ring, MR_D calculated 44.69) in the IR spectrum (Fig. 2, *A*) gives bands $\nu_{C=O}$

Fig. 2. IR spectra: product of the fractions of zone B (A), fraction No. 20 of zone D (B), caren-4(7)-ol-3 (C), and caren-4(7)-one-3 (D).

Figure 2: Fig. 2. IR spectra: product of the fractions of zone B (A), fraction No. 20 of zone D (B), caren-4(7)-ol-3 (C), and caren-4(7)-one-3 (D).

1725 cm^{-1} and $\nu_{\mathrm{C-H}}$ 2708 cm^{-1}, which indicates the presence in them of an aldehyde (^{4}). The aldehyde readily forms a semicarbazone with m.p. 192-193°. However, it was not possible to isolate it in pure form by hydrolysis of the semicarbazone. The hydrolysis product proved to be a nonhomogeneous substance: on distillation on a rectification column

it was separated into a series of fractions with somewhat differing constants. The starting aldehyde was identified in all these fractions (semicarbazone, m.p. 192-193°; bands $\nu_{\mathrm{C=O}}$ 1725 cm^{-1}, $\nu_{\mathrm{C-H}}$ 2708 cm^{-1} in the IR spectra). Fractions of zone *C* contain *l*-caranone-3 $^{(5,6)}$ (band $\nu_{\mathrm{C=O}}$ 1710 cm^{-1} in the IR spectrum; semicarbazone, m.p. 200-201°). Fractions of zone *D* consist of

Fig. 2. IR spectra: product of the fractions of zone *B* (*A*), fraction No. 20 of zone *D* (*B*), caren-4(7)-ol-3 (*C*) and caren-4(7)-one-3 (*D*).

the acetate of an unsaturated bicyclic alcohol $^{(2)}$ and, as an impurity, contain a third isomerization product of Δ^3-carene oxide. In the IR spectra of the fractions of zone *D* there are absorption bands in the region 1670-1682 cm^{-1} (Fig. 2, *B*, gives the IR spectrum of fraction No. 20), which, from the intensity of absorption, may more likely be assigned to $\nu_{\mathrm{C=O}}$ of an α,β-unsaturated ketone or aldehyde than to valence vibrations of a C=C double bond. The presence in the IR spectra of the fractions of zone *D* of a $\nu_{\mathrm{C-H}}$ band at 2737 cm^{-1} indicates that this isomerization product of the oxide is an aldehyde. The aldehyde forms a 2,4-dinitrophenylhydrazone with m.p. 166-166.5° and a semicarbazone with m.p. 211-213°. The band corresponding to $\nu_{\mathrm{C=O}}$ of the unsaturated aldehyde in the IR spectra of the saponification products of the fractions of zone *D* has a somewhat lower frequency, 1665 cm^{-1}, characteristic of the absorption of unsaturated aldehydes.

with a CO group conjugated with two double bonds. However, these data of the IR spectra concerning α,β-γ,δ-unsaturation of the aldehyde under study must be used with caution, since we are dealing not with an individual compound, but with mixtures containing it in varying amounts; all the more so because the UV spectrum data for the aldehyde 2,4-dinitrophenylhydrazone ($\lambda_{\max}$ 367, ε 32 000, isooctane) indicate rather the presence of conjugation of the CO group with only one double bond (^{7}). Thus, under the action of acetic anhydride, Δ^3-carene oxide is isomerized into *l*-caranone-3, a saturated aldehyde and an unsaturated aldehyde. The latter is not identical with the "unsaturated aldehyde of unestablished structure" which forms a semicarbazone with m.p. 223-224° (^{2,3}). In 1963 we showed (^{8}) that the "unsaturated aldehyde of unestablished structure" is a mixture of a saturated aldehyde, characterized by a semicarbazone reaction scheme with structures labeled (I), (II), (III), and (IV)

Figure 3: reaction scheme with structures labeled (I), (II), (III), and (IV)

with m.p. 192-193°, *l*-caranone-3, *l*-isocaranone-3 and carenol-3, while the semicarbazone with m.p. 223-224° is formed by *l*-isocaranone-3. In the present work *l*-isocaranone-3 was not detected.

As already noted, the fractions of zone D contain the acetate of an unsaturated bicyclic alcohol. Establishing the structure of the acetate was reduced to a choice between two possible structures for it: caren-4(7)-ol-3 acetate and caren-4-one-3 acetate, i.e. to determining the nature of the double bond; the latter was not difficult to do with the aid of IR spectra, since the semicyclic double bond of carenol acetate II and the endocyclic one of carenol acetate III have different characteristic frequencies in the IR spectrum. Since

the bicyclic acetate isolated by fractionation of the reaction mixture is contaminated with unsaturated aldehyde absorbing in the same region of the IR spectrum, the saponification product of the acetate—carenol, isolated in pure form from its 3,5-dinitrobenzoate with m.p. 105-107° (^{2})—was used for structural analysis by IR spectroscopy. In the IR spectrum of carenol (Fig. 2, B), the characteristic bands proved to be 1654 and 903 cm^{-1}, corresponding to $\nu_{\text{C=C}}$ and $\delta_{\text{C-H}}$ of $\text{CH}_2\text{=C}$ groups. Consequently, the IR spectrum data for carenol speak in favor of a structure with a semicyclic double bond. This structure is also confirmed by the formation, upon oxidation of carenol with chromic acid (^{9}), of an unsaturated bicyclic ketone (b.p. 95-97°/11 mm, n_D^{20} 1.4980, d_4^{20} 0.9853, $[\alpha]_D = -88.5°$).

In the IR spectrum (Fig. 2, G), the oxidation product gives, in addition to bands at 1653 and 886 cm^{-1}, an intense band corresponding to the stretching vibrations of the CO group of cyclohexenones conjugated with one double bond (^{4}). If the alcohol had the structure of caren-4-ol-3, it is unlikely that the carene structure would have been retained in its oxidation product. It is known that in those cases where unsaturated ketones of the carene series with an endocyclic double bond should be formed, the final products obtained are cycloheptadienones (^{10}) or cyclohexadienones (^{8}), absorbing in the region of lower frequencies, 1670-1663 cm^{-1}. Thus, the acetate of the bi-

the structure of caren-4(7)-ol-3 acetate should be assigned to the cyclic unsaturated alcohol.

As can be seen from Fig. 1, the α_D values of the fractions of zone F reach the maximum value of (+)-rotation (the other constants change only slightly). According to elemental analysis, the fractions contain a product of composition $C_{12}H_{18}O_2$. From the constants and the IR spectrum, the product proved to be close to the acetate of the monocyclic dienic alcohol—*n*-menthadien-1,5-ol-8—from the oxidation reaction of Δ^3-carene with lead tetraacetate and mercury acetate (^{10}). Study of the chemical properties of the acetate of zone

F confirmed its identity with *n*-menthadien-1,5-ol-8 acetate. Thus, the acetate of zone *F* forms the same adducts with maleic anhydride (m.p. 146-146.5°) and α-naphthoquinone (m.p. 69.5-71°) as does *n*-menthadien-1,5-ol-8 acetate. The saponification product of the acetate under study (b.p. 66.5-67°/2 mm, n_D^{20} 1.4983, d_4^{20} 0.9578, $[\alpha]_D = +100.5°$) gives the same adduct with α-naphthoquinone (m.p. 124.5-125.5°) and the same 3,5-dinitrobenzoate (m.p. 93-94°) as *n*-menthadien-1,5-ol-8. The formation of *n*-menthadien-1,5-ol-8 acetate (IV) in this reaction can apparently be explained as follows. Caren-4-ol-3 acetate—the product of stabilization of bicyclic carbocation I by elimination of a β-proton from the $C_{(5)}H_2$ group under the reaction conditions—undergoes an allylic rearrangement of the type of allylic rearrangement of 1,3-diene systems with displacement of the functional group into the δ-position ([11–14]). The conjugated system here is represented by a double bond and a three-membered ring possessing unsaturation close to that of a double bond ([15,16]). The peculiarity of such a conjugated system causes the formation of a nonallylic acetate as a result of allylic rearrangement. Displacement of one double bond of the conjugated system is accompanied by displacement of the second unsaturated unit —the three-membered ring—which leads to its rupture and the formation of a double bond conjugated with the first; the δ-position becomes the position at $C_{(8)}$, to which the acetoxy group also migrates.

The discrepancy in the data concerning the nature of the unsaturated acetate reported in communications ([1],[2]) is now easily explained: in the first work, a mixture of bicyclic and monocyclic acetates was in fact investigated. Naturally, the *n*-menthadien-1,5-ol-8 acetate present in the mixture gave an adduct with maleic anhydride. On this basis the acetate $C_{12}H_{18}O_2$ as a whole was regarded as the acetate of a monocyclic dienol. In the second work, by fractionation of the acetate $C_{12}H_{18}O_2$, or "monoacetate," on a rectification column, an unsaturated bicyclic acetate was isolated, and no attention was paid to smaller amounts of the acetate of a monocyclic dienol.*

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Received
3 VII 1964

CITED LITERATURE

1. B. A. Arbuzov, Z. G. Isaeva, ZhOKh, **24**, 1250 (1954).
2. B. A. Arbuzov, Z. G. Isaeva, DAN, **122**, 73 (1958).
3. B. A. Arbuzov, *Investigations in the Field of Isomeric Transformations of Bicyclic Terpene Hydrocarbons and Their Oxides.* Dissertation, Kazan,

1936, p. 161.

4. L. Bellamy, *The Infrared Spectra of Complex Molecules*, Moscow, 1963.
5. H. Kuczyński, Z. Chabudziński, Roczn. Chem., **29**, 437 (1955).
6. B. A. Arbuzov, Z. G. Isaeva, DAN, **121**, 105 (1958).
7. I. N. Nazarov, L. A. Kazitsyna, I. I. Zaretskaya, ZhOKh, **27**, 606 (1957).
8. Z. G. Isaeva, I. S. Andreeva, DAN, **152**, No. 1, 106 (1963).
9. H. C. Brown, C. Garg, J. Am. Chem. Soc., **83**, 295 (1961).
10. V. V. Ratner, *Isomeric Transformations of* Δ^3*-Carene in Some Oxidation Reactions.* Dissertation, Kazan, 1963.
11. I. N. Nazarov, L. B. Fisher, Izv. AN SSSR, OKhN, 1945, 631.
12. I. N. Nazarov, L. B. Fisher, ZhOKh, **20**, 1114 (1950).
13. I. N. Nazarov, L. B. Fisher, Izv. AN SSSR, OKhN, 1948, 427, 436.
14. J. M. Shackelford, L. H. Schwartzman, J. Org. Chem., **27**, 1047 (1962).
15. M. Yu. Lukina, Usp. Khim., **31**, 901 (1962).
16. O. A. Nesmeyanova, M. Yu. Lukina, B. A. Kazanskii, DAN, **153**, 114, 357 (1963).

* It should be noted that the fractions of the intermediate zone E consist mainly of caren-4(7)-ol-3 acetate.

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

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