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Abstract

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On the Products of the Reaction of the Oxides of α-Pinene and Δ^3-Carene with Acetic Anhydride

In 1953, as a continuation of work on the study of isomeric transformations of the oxides of bicyclic terpene hydrocarbons, we began an investigation of the reaction of the oxides of α-pinene, Δ^3-carene, and camphene with acetic anhydride.

It was shown that the reaction of bicyclic terpene oxides with acetic anhydride proceeds in a complex manner, with the formation of mixtures of products, and is accompanied by isomerization of the oxides.

Under the action of acetic anhydride, camphene oxide gives camphenylic aldehyde, the acetate of the enol form of camphenylic aldehyde, and 2,10-camphanediol diacetate. From the products of the reaction of α-pinene oxide with acetic anhydride, three substances were likewise isolated: campholenic aldehyde, sobrerol diacetate, and the acetate of an unsaturated alcohol of composition $C_{12}H_{18}O_2$. An analogous product was also obtained from Δ^3-carene oxide (together with β-caranediol diacetate). Their structure had not been established by us.

The aim of the present work was to elucidate the structure of the acetates from the oxides of α-pinene and Δ^3-carene.

Recently, reports by A. Kergomard have appeared on the study of the action of acetic anhydride on limonene oxide ([1]) and on the synthesis of perillyl alcohol ([2]), which was based on the reaction of β-pinene oxide with acetic anhydride. Since these works are close in character to our investigations of the isomeric transformations of bicyclic terpene oxides in the reaction with acetic anhydride, we publish the data obtained to date on the study of the structure of the above-mentioned acetates. As was already indicated earlier ([3]), the yield of acetate $C_{12}H_{18}O_2$ does not exceed 30% for α-pinene oxide and 22% in the case of Δ^3-carene oxide. According to the scheme we proposed for the mechanism of the reaction of oxides with acetic anhydride, it might have been expected that formation of acetates $C_{12}H_{18}O_2$ would become the predominant direction of the reaction in the presence of a substance that binds acetate ions and, consequently, reduces to a minimum the reaction leading to acetate-diols. In order to test this supposition and to obtain acetate $C_{12}H_{18}O_2$ in higher yield, the reaction of α-pinene oxide with acetic anhydride was carried out in the pres-

reaction scheme showing formation of products (I)-(VI) from α-pinene oxide with acetic anhydride

Figure 1: reaction scheme showing formation of products (I)-(VI) from α-pinene oxide with acetic anhydride

ence of $NaHCO_3$. The experiment showed that 40% of the α-pinene oxide was recovered unchanged; the isomerization reaction of the oxide to campholenic aldehyde proceeded to a considerably lesser extent. But instead of the expected acetate, from the reaction products there was isolated, in 28% yield, an alcohol of composition $C_{10}H_{16}O$ with the constants: b.p. 93.5-96°/6 mm, n_D^{20} 1.4972, d_4^{20} 0.9544, MR_{found} 46.62, $C_{10}H_{16}O\,|=_2\ MR_{\text{calc.}}$ 46.77, identical with *dl*-trans-carveol ([4]). Acid phthalate, m.p. 136-137°; literature data ([5]): m.p. of the acid phthalate of *dl*-carveol 136-136.5°. The 3,5-dinitrobenzoate was obtained with an indistinct m.p. of 108-113°, despite numerous recrystallizations; m.p. of the 3,5-dinitrobenzoate of *dl*-trans-carveol 119°, of *dl*-cis-carveol 91.5° ([4]).

On oxidation of the alcohol with chromic anhydride in acetic acid, carvone was obtained: b.p. 94-97°/6.5 mm, n_D^{20} 1.4955; d_4^{20} 0.9663, MR_{found} 45.30; $C_{10}H_{14}O\,|=_2\ MR_{\text{calc.}}$ 45.26; yield 47%. Carvone was identified.

with the preparation of a hydrogen sulfide compound with m.p. 189-191° (m.p. of the H_2S compound of *dl*-carvone 189-190° ([5])).

From the data given in work ([3]), it is evident that the boiling point of the acetate $C_{12}H_{18}O_2$ from α-pinene oxide lies within a broad temperature range. In order to isolate individual products, the reaction mixture from α-pinene oxide and acetic anhydride was repeatedly fractionated on a column with an efficiency of 27 theoretical plates. In addition to campholenic aldehyde and sobrerol acetate, we isolated three substances of one and the same composition, $C_{12}H_{18}O_2$,* with a total yield of 31%.

1. The lower-boiling product (33.3% of the total weight of the $C_{12}H_{18}O_2$ products) had the following constants: 79-80°/3 mm, n_D^{20} 1.4783, d_4^{20} 0.9921, $[\alpha]_D = +7^\circ$ (c 2.85, ethanol). MR_{found} 55.38; $C_{12}H_{18}O_2| = 1$, 4-membered ring, $MR_{\text{calc.}}$ 55.10. Titration with perphthalic acid showed that the product molecule contains one double bond.

On saponification with 7% aqueous-alcoholic NaOH solution, an alcohol $C_{10}H_{16}O$ was obtained with the constants: b.p. 67.5-70°/2.5 mm, n_D^{20} 1.4992, d_4^{20} 0.9777, $[\alpha]_D = -50.1^\circ$ (c 1.9, ethanol), MR_{found} 45.66, $C_{10}H_{16}O| = 1$, 4-membered ring, $MR_{\text{calc.}}$ 45.50.

3,5-Dinitrobenzoate, m.p. 122-123.5°; phenylurethane, m.p. 96-97.5°; *p*-nitrobenzoate, m.p. 66.5-68°. According to the "ion-pair" scheme of the mechanism of reaction of α-oxides proposed by us earlier ([6]), in the interaction of α-pinene oxide with acetic anhydride one may expect the formation of the following products:

* Experiments on preparing adducts of the acetates $C_{12}H_{18}O_2$ from α-pinene and Δ^3-carene oxides with maleic anhydride ([3]) could not be reproduced.

Consequently, the bicyclic unsaturated alcohol with one double bond in the molecule which we isolated may be identical with one of the pinocarveols (II). From the boiling point, n_D^{20}, d_4^{20}, and $[\alpha]_D$, the alcohol is more likely identical with trans-pinocarveol ([7]). However, there is no complete agreement in the data for crystalline derivatives: according to ([7]), the m.p. of the phenylurethane of trans-pinocarveol is 96–97°, and the m.p. of the *n*-nitrobenzoate is 93.5–94.5°. According to Schmidt ([8]), the phenylurethane of trans-pinocarveol melts at 88–90°; upon hydration with dilute sulfuric acid, trans-pinocarveol forms a hydrate with m.p. 190–191°, which we were unable to obtain. cis-Pinocarveol does not form a hydrate, but also does not give many other derivatives; it forms an *n*-nitrobenzoate with m.p. 104° ([9]). The acetate of a bicyclic unsaturated alcohol isolated by us may have structure (III). In the literature we found no data either on the acetate or on the corresponding alcohol of the indicated structure.

2. Constants of the second product, $C_{12}H_{18}O_2$, from the reaction of α-pinene oxide with acetic anhydride (relative content in the mixture of products $C_{12}H_{18}O_2$ 46.5%): b.p. 87–87.5°/3 mm, n_D^{20} 1.4747, d_4^{20} 0.9707, $[\alpha]_D = +100.5^\circ$ (c 1.86, ethanol), MR_{found} 56.24, $C_{12}H_{18}O_2F_2$ MR_{calc} 56.14. According to titration with perphthalic acid, the product contains 2 double bonds in the molecule.

By saponification with aqueous alcoholic NaOH solution (10%), an alcohol $C_{10}H_{16}O$ was obtained from the acetate (yield 89.2%) with constants: b.p. 86–87°/3 mm, n_D^{20} 1.4954, d_4^{20} 0.9510, $[\alpha]_D = +115.6^\circ$ (c 2.77, ethanol), MR_{found} 46.65, $C_{10}H_{16}OF_2$ MR_{calc} 46.77; 3,5-dinitrobenzoate, m.p. 120–121°; *n*-nitrobenzoate, m.p. 101.5–102.5°.

In the reaction of α-pinene oxide with acetic anhydride, the formation of two acetates of monocyclic alcohols may be expected: carveol acetate (IV) and the acetate of structure (V). Comparison with the literature data shows that, by its constants, the alcohol described is close to trans-carveol. However, the 3,5-dinitrobenzoate and *n*-nitrobenzoate differ strongly in m.p. from the corresponding derivatives of trans-carveol.

Upon oxidation of the alcohol with chromic anhydride in acetic acid, a ketone was obtained in 49% yield with constants: b.p. 86.5–88°/6 mm, n_D^{20} 1.4949, d_4^{20} 0.9659, $[\alpha]_D = +24.97^\circ$ (c 3.78, ethanol); MR_{found} 45.31; $C_{10}H_{14}OF_2$ MR_{calc} 45.26. Phenylhydrazone, m.p. 108–108.5°; a mixed sample with the phenylhydrazone of *d*-carvone, m.p. 107–108°, melted without depression, m.p. (106.5–108°).

3. The third product of composition $C_{12}H_{18}O_2$ (relative yield 20.1%) had constants: b.p. 89–89.5°/3 mm, n_D^{20} 1.4844, d_4^{20} 0.9809, $[\alpha]_D = +23.50^\circ$ (c 1.75, ethanol), MR_{found} 56.61, $C_{12}H_{18}O_2F_2$ MR_{calc} 56.14. Its investigation is continuing.

An investigation of the composition of the products from the interaction of Δ^3-carene oxide with acetic anhydride showed that the reaction does not proceed smoothly. The composition of the reaction products (yield given calculated on the oxide taken into the reaction) was: 1) hydrocarbon fractions with n_D^{20} 1.4875-1.4913, d_4^{20} 0.8615-0.8787, 3.5%; 2) carbonyl-containing products, 7%; 3) acetate $C_{12}H_{18}O_2$, 14%; 4) β-carenglycol diacetate, 13%.

In the reaction, apparently, two carbonyl compounds are formed: 2 semicarbazones were obtained with m.p. 205-207 and 222-224° (with decomposition). Acetate $C_{12}H_{18}O_2$ (see above) had constants: b.p. 86.5°/3.5 mm, n_D^{20} 1.4746, d_4^{20} 0.9864, $[\alpha]_D = -44.01^\circ$ (c 4.17, ethanol), MR_{found} 55.33; $C_{12}H_{18}O_2F_1$, 3-membered ring, MR_{calc} 55.10. The presence of 1 double bond in the molecule was established by titration with perphthalic acid. Upon saponification of the product with aqueous alcoholic alkali (4.5%), an alcohol was obtained with constants: b.p. 69-72°/2.5 mm, n_D^{20} 1.4953, d_4^{20} 0.9660, $[\alpha]_D = -41.37^\circ$ (c 4.84, ethanol), MR_{found} 45.91, $C_{10}H_{16}OF_1$, 3-membered ring, MR_{calc} 45.73; 3,5-dinitrobenzoate, m.p. 106-107°. The alcohol rapidly crystallized on seeding with the crystalline product of saponification of the acetate $C_{12}H_{18}O_2$, obtained in one of the experiments by purification through the 3,5-dinitrobenzoate (b.p. 100-103°/9 mm, m.p. 55-56°).

According to the "onium" scheme for the mechanism of the reaction of Δ^3-carene oxide with acetic anhydride, the formation of two acetates of unsaturated bicyclic alcohols may be represented as follows:

[scheme: Δ^3-carene oxide $\xrightarrow{(CH_3CO)_2O}$ onium acetate intermediate*arrow*allylic cation acetate intermediate $\xrightarrow[-H^+]{}$ acetate (I) and $\xrightarrow[-H^+]{}$ acetate (II)]

D. Tishchenko, A. Khovanskaya, and T. Danilova[11] assign structure (II) to carenol acetate, obtained by them from 3-chloro-Δ^4-carene by the action of potassium acetate. Carenol acetate and the acetate from Δ^3-carene oxide differ greatly in n_D^{20} (1.4820 and 1.4746). The alcohols—the products of alkaline saponification—have the following constants: carenol—b.p. 80-81°/0.7 mm, n_D^{20} 1.4987, d_4^{20} 0.967. The alcohol from Δ^3-carene oxide—b.p. 69-72°/2.5 mm, n_D^{20} 1.4957, d_4^{20} 0.9660.

On treatment of the alcohol from Δ^3-carene oxide with phenyl isocyanate, two products were isolated: 1) with m.p. 96-97° and 2) in smaller amount with m.p. 106-107°. Study of the reaction products is continuing.

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