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Abstract

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ON THE PRODUCTS OF AUTOXIDATION OF Δ^3-CARENE

At the present time it is generally known that the primary products of the autoxidation of unsaturated hydrocarbons are unsaturated hydroperoxides with an HOO group in the α-position to the double bond.

The process of autoxidation of unsaturated hydrocarbons, especially terpene hydrocarbons, proceeds in a complex manner; the hydroperoxides formed under the reaction conditions undergo further transformations: decomposition, interaction with the initial hydrocarbons, isomerization, etc.

Among terpene hydrocarbons, α- and β-pinenes have been studied rather fully in this respect. In the products of their autoxidation and in the products of reduction of the latter, the corresponding hydroperoxides, ketones, alcohols, oxides, and hydrocarbons have been identified. Very few works have been devoted to the autoxidation of Δ^3-carene. Owen and Simonsen ([1]) found that, on oxidation of Δ^3-carene with moist oxygen in the presence of cobalt resinate and subsequent steam distillation of the reaction products, alcohols of composition $C_{10}H_{16}O$ and ketones $C_{10}H_{14}O$ are formed in approximately equal amounts. However, their structure was not established. Blom and Widmark ([2]) studied the kinetics of the autoxidation of Δ^3-carene.

In 1956 Erofeev and Chirko ([3]), in the catalytic autoxidation of Δ^3-carene, obtained "Δ^3-carene hydroperoxide," and, by reducing it with potassium iodide in acetic acid, an alcohol to which they assigned the structure of Δ^3-caren-2-ol, at the same time identifying it with carenol obtained by Tishchenko ([4]) from 3-chlorocarene-4 through the corresponding acetate and having the structure of Δ^4-caren-3-ol. The sharp discrepancy in the data of Simonsen and of Erofeev and Chirko on the course of the autoxidation reaction of Δ^3-carene is noteworthy; in the light of literature data on the complexity of the products of autoxidation of unsaturated hydrocarbons, the so unambiguous course of the oxidation reaction of Δ^3-carene in the experiments ([3]) seems surprising.

In the present work we began a study of the products of autoxidation of Δ^3-carene formed upon oxidation of the latter with oxygen in the presence of catalysts (lead acetate, manganese dioxide). By analogy with the data of Blom and Seytshel ([5]), Suzuki ([6]), Schmidt ([7]), Schenck, Eggert and Denk ([8]), Mura, Golumbic and Fisher ([9]) on the autoxidation of α- and β-pinenes, and the data

structural formulas of possible hydroperoxides of Δ^3-carene

Figure 1: structural formulas of possible hydroperoxides of Δ^3-carene

of Farmer, Koch and Sutton ([10,11]) on the migration of double bonds accompanying the formation of unsaturated hydroperoxides, and taking into account that in the molecule of Δ^3-carene there are three "points of attack" in the autoxidation reaction (two CH_2 groups and one CH_3 group in the α-position to the double bond), it may be assumed a priori that the reaction of oxidation of Δ^3-carene with oxygen will not proceed unambiguously. Formation of the following hydroperoxides may be expected:

and, upon reduction of them, the corresponding alcohols, ketones

[structural formulas]

and hydrocarbons—the products of decomposition of the hydroperoxides. Our very first experiments already confirmed this supposition concerning the complexity of the autoxidation process of Δ^3-carene.

Autoxidation of Δ^3-carene was carried out by passing oxygen through the hydrocarbon (with simultaneous vigorous stirring in order to agitate the catalyst) until the content of active oxygen in 1 ml of the reaction mixture reached a constant value (0.1422–0.1465 g of hydroperoxide of composition $C_{10}H_{16}O_2$ in 1 ml of the reaction mixture).

Contrary to the data of Erofeev and Chirko, we were unable to isolate "Δ^3-carene hydroperoxide" in pure form; during distillation of the autoxidation products in a high vacuum (0.025 mm), i.e., under the same conditions as in their experiments, decomposition of the hydroperoxide occurred, and the distilled product contained four times less hydroperoxide than the undistilled product.

The reaction mixture from the autoxidation reaction, after removal of the bulk of the unreacted Δ^3-carene, was reduced with sodium sulfite and fractionated on a column with an efficiency of 17 theoretical plates. Composition of the distillate: 1) hydrocarbon fractions of composition $C_{10}H_{14}$ with n_D^{20} 1.4940–1.5010; d_4^{20} 0.8338–0.8656, 30%; 2) ketone fractions with n_D^{20} 1.4850–1.4929; d_4^{20} 0.9193–0.9380, 29%; 3) alcohol fractions with n_D^{20} 1.4952–1.5039; d_4^{20} 0.9530–0.9747, 41%.

In the IR spectrum of the ketone fractions there is a band at 1656 cm^{-1}, characteristic of a $C = O$ group conjugated with two double bonds. From the melting points of the crystalline derivatives—semicarbazone 182–184°, 2,4-dinitrophenylhydrazone 149.5–150.5°—the ketone proved to be identical with eucarvone (m.p.: semicarbazone 183–185° (12), 2,4-dinitrophenylhydrazone 152–153° (13)), i.e., the dienone ketone of the cyclopentane series, 2,6,6-trimethylcycloheptadien-2,4-one-1. The IR spectrum of eucarvone has the corresponding absorption band of the $C = O$ group at 1660 cm^{-1}.

structural formulas I, II, and III

Figure 2: structural formulas I, II, and III

The alcohol fractions of the reduction products of the autoxidate of Δ^3-carene contain dextrorotatory and levorotatory alcohols of composition $C_{10}H_{16}O$.

On treatment of the levorotatory alcohol (b.p. 62-64°/2 mm, n_D^{20} 1.4990, d_4^{20} 0.9754, $\alpha_D = -51.5^\circ$, MR found 45.76, $C_{10}H_{16}O$ [F 1,3-membered ring, MR calculated 45.74]) with p-nitrobenzoyl chloride, a p-nitrobenzoate of m.p. 154-155° was obtained. A mixed sample with the p-nitrobenzoate of carenol (m.p. 155-156°, m.p. of the 3,5-dinitrobenzoate 106-107°), which we had obtained earlier (14) by the reaction of Δ^3-carene oxide with acetic anhydride, gave no depression of the melting point. Consequently, the alcohol from the autoxidation reaction of Δ^3-carene is identical with carenol, to which, on the basis of analysis of the IR spectra (presence of bands characteristic of $C=C$ and $C-H$ valence vibrations at 1640 cm^{-1}, 890 cm^{-1}), we assign the structure caren-4(7)-ol-3

[structural formula]

The formation of the hydroperoxide corresponding to it is accompanied by migration of the double bond, which has already been observed in the photosensitized oxidation of α- and β-pinenes (8).

The dextrorotatory alcohol (b.p. 69-70°/1.5 mm, n_D^{20} 1.5026, d_4^{20} 0.9550, $\alpha_D = +55^\circ$, MR found 47.01, $C_{10}H_{16}O$ [F_2 calculated 46.77]) forms a p-nitrobenzoate of m.p. 94-95.5° and a 3,5-dinitrobenzoate of m.p. 90.5-92°.

In its IR spectrum there are absorption bands at 1593 cm^{-1}, 1639 cm^{-1}, characteristic of a conjugated system of double bonds. The presence of conjugated double bonds in the alcohol molecule is also confirmed by the data of Raman spectra, in which the frequencies 1593 cm^{-1} ([10]), 1643 cm^{-1} ([7]), 1658 cm^{-1} ([7]) are present. Terephthalic acid titrates 1.5 double bonds. These data indicate a monocyclic structure of the alcohol, namely cycloheptadienic.

One of two possible structures may be assigned to the alcohol:

2,6,6-trimethylcycloheptadien-2,4-ol-1 (eucarveol) (I) or 3,6,6-trimethylcycloheptadien-2,4-ol-1 (II).

However, structure I is excluded, since on oxidation of the alcohol with a chromic anhydride–pyridine complex a ketone was obtained with constants: 66–70°/3 mm, n_D^{20} 1.5098, d_4^{20} 0.9588, $\alpha_D = +84.5^\circ$, not identical with eucarvone. By the melting point of the 2,4-dinitrophenylhydrazone (171–173°), the product of oxidation of the alcohol is identical with an isomer of eucarvone described by Campbell et al. ([13]) (m.p. of the 2,4-dinitrophenylhydrazone 172–173°), the structure of which the authors did not establish.

The IR spectrum of the product of oxidation of the alcohol has an absorption band at 1657 cm^{-1}, characteristic of a C = O group conjugated with two double

structural formula of caradiene-2,4(7)

Figure 3: structural formula of caradiene-2,4(7)

bonds. The IR spectrum of the eucarvone isomer has a close absorption band at 1668 cm^{-1} ([13]). According to the data of the authors ([13]), the eucarvone isomer on oxidation with $KMnO_4$ gives α,α-dimethylsuccinic acid, which is also in agreement with the structures II and III accepted by us for the alcohol and ketone, respectively.

The hydrocarbon fractions of the products of autoxidation of Δ^3-carene have been studied by us to a considerably lesser extent than the other products of autoxidation.

In the IR spectrum of one of them, of composition $C_{10}H_{14}$, purified by chromatography on alumina (III, alkaline) and having constants: b.p. 52.5 –54.5°/11.5 mm, n_D^{20} 1.4941, d_4^{20} 0.8656, $\alpha_D = +3.3°$, MR found 45.07, $C_{10}H_{14}F_2$ calculated 43.74, exaltation 1.33–there are absorption bands at 1640, 1603, 890 cm^{-1}, indicating the presence of a conjugated semicyclic double bond (see, for example, ([15])). By analogy with the corresponding product from the autoxidation reaction of α-pinene, verbenene ([9]), this diene hydrocarbon may be assigned the structure caradiene-2,4 (7).

The possibility is not excluded that hydrocarbons of a cycloheptatriene nature are also present in the hydrocarbon fractions. On oxidation of the hydrocarbon fractions with chromic anhydride, terephthalic acid was not obtained; consequently, cymene is absent from them.

Thus, summarizing the foregoing, it may be said that the molecule of Δ^3-carene has three "points of oxidative attack" : the CH_3 group and two CH_2 groups located in the α-position to the double bond, which is confirmed by the structure of the products isolated by us: caren-4(7)-ol-3, eucarvone, and 3,6,6-trimethylcycloheptadien-2,4-ol-1. The formation of these products is accompanied by isomeric transformations: displacement of the double bond from the endo- to the semicyclic position or expansion of the six-membered ring to a seven-membered one. In the course of the autoxidation reaction it is also possible to form

formation of the ketone 3,6,6-trimethylcycloheptadien-2,4-one-1 (an isomer of eucarvone) and of the corresponding eucarvone alcohol, 2,6,6-trimethylcycloheptadien-2,4-ol-1, which we have not yet isolated.

Work on studying the composition and structure of the autoxidation products of Δ^3-carene is continuing.

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