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The liquid-phase oxidation of 3-carene in the presence of various catalytic systems has been studied. The possibility has been shown of the directed preparation of 3-carene oxide, of ketones with a carane skeleton and a 7-membered ring, or of aromatic tertiary alcohols.

The study of the liquid-phase oxidation of the monoterpene hydrocarbon 3-carene (one of the main components of domestic turpentines) is of interest from both the theoretical and the practical points of view. The presence in the 3-carene molecule of two reactive centers leads to the occurrence of a number of skeletal transformations of the bicyclo[4.1.0]-heptane structure.

According to the literature [1-18], the main products of the oxidation of 3-carene are alcohols and ketones with bicyclo[4.1.0]heptane, trimethylcycloheptane, and p- and m-methane structures. By varying the conditions of the reaction it is possible to obtain products containing predominantly compounds with one of the above-mentioned skeletons [1, 14, 16]. Practical interest is presented by, for example, 3-caren-5-one (I) - an intermediate in the synthesis of the pyrethroids [1], 2-caren-4-one (II) - the starting material for carbone [19], and 3,6- and 2,6-trimethylcyclopenta-2,4-dienones ((III) and (IV), respectively) recognized odoriferous substances [20]. However, information on the composition of the oxidate given in different publications is contradictory.

The present investigation was devoted to establishing the composition of the neutral products of the liquid-phase oxidation of 3-carene in the presence of various catalytic systems.

The 3-carene was oxidized by molecular oxygen using known catalysts for the oxidation of hydrocarbons [21]. The characteristics of the initial additives and the conditions of performing the reaction are given in Table 1. The oxidates were distilled under vacuum. As shown by GLC analysis, the oxygen-containing fractions with bp 75-120°C (5 mm) contained 37 components, of which the main 20 were identified: ketones (I-IV), 3-caren-2-one (V), 3-carene-2,5-dione (VI), 3,4- $\alpha$ -epoxycarane (VII), 3-formyl-3,6,6-trimethylbicyclo[3.1.0]hexane (VIII), 3-hydroxymethyl-3,6,6-trimethylbicyclo[3.1.0]hexane (IX), carane-3,4-diol (X), 3-caren-2-ol (XI), 2-caren-4-ol (XII), 3(10)-caren-4-ol (XIII), 4-caren-3-ol (XIV), p-cymen-8-ol (XV), m-cymen-8-ol (XVI),  $\alpha$ -terpineol (XVII), silveterpinenol (XVIII), p-mentha-2,6-dien-8-ol (XIX), and m-mentha-4,5-diene-8-ol (XX). Quantitative compositions of the oxygen-containing fractions as functions of the reaction conditions are given in Table 2. The isolation of the individual components (I-VIII) and (XV-XVIII) was achieved by the PGLC method, and their identification by the GLC method using phases of different polarities and by spectral methods.

The composition of the oxidate showed that, in addition to the oxidation of 3-carene, secondary transformations took place during the reaction — the disproportionation of hydrogen in the products formed and rearrangements of the hydrocarbon skeleton. The presence of comparable amount sof the ketones (I), (II), and (V), and of the epoxide (VII) in the oxidate showed that the primary process of the oxidation of 3-carene took place in two independent directions, the first being the allyl oxidation of the methylene groups, and the second the addition of oxidation to the double bond.

It is known [22] that the allyl oxidation of the methylene groups of 3-carene under the conditions of a free-radical reaction leads to hydroperoxides and dialkyl peroxides. The decomposition of the hydroperoxides forms the ketones (I), (II), and (V) and the alcohol

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| TABLE       | 1. Rea         | ction C | Conditic              | ons for      | the Li                   | quid-Phas            | e Oxidat    | tion   | of 3-Ca     | rene                  |       |      |      |                  |
|-------------|----------------|---------|-----------------------|--------------|--------------------------|----------------------|-------------|--------|-------------|-----------------------|-------|------|------|------------------|
| Experi-     | Temper-        | Time,   |                       |              |                          | Cat                  | alytic sy   | stem ( | component   | s - moles/1           | iter) |      |      |                  |
| ment<br>No. | ature, :<br>°C | min     | Co (OAc) <sub>3</sub> | Co<br>salen* | Co na-<br>phthe-<br>nate | C¢<br>stearate       | Mn (OAc).   | NaOH   | NaBr        | o-Phe-<br>nanthroline | нсо,н | Асон | EtOH | 0 <sup>°</sup> H |
|             | 20             | 360     | $2.10^{-2}$           | 1            | 1                        | 1                    | 1.10-3      |        | 4.10-2      | ł                     |       | 1    | 1    | !<br><b>]</b>    |
| 2           | 70             | 360     | $2.10^{-2}$           | ļ            | }                        | I                    | ł           | 1      | $4.10^{-2}$ | 1                     | 1     | 8,7  | ſ    | 1                |
| e           | 20             | 360     | 2.10-3                | 1            | 1                        | 1                    | $2.10^{-3}$ | ۱      | $4.10^{-2}$ | 1                     | [     | 8,7  |      | ١                |
| 4           | 53             | 330     | $2.10^{-2}$           | 1            | ł                        | I                    | $2.10^{-3}$ | 1      | $4.10^{-2}$ | i                     | 1     | 8,7  | 1    | I                |
| ŝ           | 0%             | 360     | $2.10^{-2}$           | 2.10-3       | ł                        | I                    | ł           | l      | $4.10^{-2}$ |                       | 1     |      | ł    | I                |
| 9           | 70             | 360     | 2.10-2                | $2.10^{-3}$  | I                        | l                    | 1           | 1      | 4.10-2      | 1                     | 1     | 8,2  | 1    | ١                |
| 7           | 70             | 360     | $2.10^{-2}$           | 2.10-3       | 1                        | 1                    | 1           | 1      | 4.10-2      | 1                     | 0,1   | 8,2  | ł    | ١                |
| ×           | 70             | 360     | $2.10^{-2}$           | 2.10-3       | 1                        | 1                    | 1           | í      | 4.10-2      | 1                     | 0,5   | 8,6  | 1    | Į                |
| 6           | 70             | 120     | 1                     | 2.10-3       | 2.10~2                   | ١                    | ł           | 1      | $4.10^{-2}$ | 1                     | 0,1   | 1    | i    | i                |
| 10          | <b>5</b> 0     | 600     | 1                     | ł            | ł                        | 1                    | ļ           | 2.0    | 1           | 1                     | 1     | 1    | ļ    | 10,0             |
| 11          | 50             | 300     | 1                     | ļ            | 1                        | I                    | 1           | 2,0    | I           | 1                     | 1     | 1    | 8,0  | I                |
| 12          | 50             | 300     | 1                     | ł            | 1                        | 1,2.10 <sup>-3</sup> | )           | 1,7    | 1           | 3,6.10 <sup>-3</sup>  | 1     | 1    |      | 10,0             |
|             |                | -       |                       | _            | _                        |                      |             |        |             |                       | _     |      | -    |                  |

\*Cobalt(II)-bis(salicylidene)ethylenediamine.

| 3-Care       |
|--------------|
| of           |
| Oxidation    |
| Liquid-Phase |
| the          |
| of           |
| Products     |
| the          |
| of           |
| Compositions |
| ABLE 2.      |

|  |                   | *                              | 2,8  | 1.3   | 6.0        | 7,3   | 7,4    | 18,8 | 15,9 | 18.0        | 9,1        | 3,2          | 8,2  | 2.9  |
|--|-------------------|--------------------------------|------|-------|------------|-------|--------|------|------|-------------|------------|--------------|------|------|
| Products of the Liquid-Phase Oxidation of 3-Carene                             |                   | ××                             | 3,3  | 1,9   | 4,1        | Tr.   | Ì      | 0,3  | Τr.  | 1           | 3,3        | 1            | Tr.  | 1    |
|  |                   | XIX                            | 2,0  | 1,4   | 3,3        | Tr.   | 1      | 0,8  | 답.   | Tr.         | 1,4        | Tr.          | Τr.  | 1    |
|  |                   | жил                            | 1,3  | 10,1  | 7,7        | 6,1   | Τr.    | 3,7  | 4,1  | 9 <b>,4</b> | 8,0        | 1,4          | 10,4 | 2,8  |
|  |                   | ли                             | 4,0  | 9,4   | 0,6        | 9'6   | Τr.    | 6,1  | 4,3  | 12,7        | <b>9'9</b> | 3 <b>.</b> 1 | 18,7 | 1,0  |
|  |                   | XVI                            | 7.7  | 12,6  | 8.3        | 6,2   | 2,9    | 6,8  | 4,5  | 13,1        | 18.1       | ц.           | 9,4  | 3,1  |
|  | ж                 | xv                             | 20,3 | 10,3  | 14,3       | 10.3  | 7,1    | 12,0 | 10,9 | 17.1        | 16,0       | Tr.          | 6*2  | 1.3  |
| ene  | tion,             | XIV                            | 2.2  | 0,4   | 5,4        | 6 1   | 3,2    | 1,4  | 2,8  | 2,1         | 4.7        | 6'0          | Τr.  | ц.   |
| S-Car  | frac              | т                              | 6,0  | 0,3   | 0,4        | 2,6   | 0,3    | Tr.  | 1,1  | Tr.         | 0, 3       | 1            |      | Ir.  |
| of 3   | ining             | XII                            | 1.1  | 0,2   | Tr.        | 2,5   | 0,1    | Tr.  | 0,5  | 1.1         | 2,4        | Τr.          | 1    | Τr.  |
| ion  | conta             | 1X                             | 0.7  | Tr.   | 0,3        | 1,9   | 1,1    | 0'0  | 0.9  | Tr.         | 0.4        | 1,3          | I    | Τr.  |
| idat   | vgen-4            | x                              | ľr.  | 0,5   | 1,4        | 3,3   | Τr.    | 0,2  | 1,4  | ,           | Ir.        | 4,5          |      | 1    |
| e Ox   | he ox             | 1X                             | 0,5  | 1     | 1,6        | 1,1   | 1.2    | Tr.  | Tr.  | Tr.         | Tr.        | 1            | 1    | ſ    |
| Phas   | of th             | шл                             | 18,5 | 2,1   |            | 1,1   | 2,0    | 20,5 | 12,1 | 1,4         | 6,4        | 1            | 0,8  | Tr.  |
| uid-   | ions              | VII                            | 2.1  | 1,0   | 0,4        | 1,6   | 24.0   | 1.1  | 7,6  | Tr.         | 1,4        |              | 1,3  | Tr.  |
| Liq  | posit             | ۲١                             | 3,3  | 19.6  | 12,0       | 6,0   | 12,1   | Τr.  | Ir.  |             | Ir.        | Tr.          | Ir.  | Tr.  |
| the  | Con               | 2                              | 2,3  | 5,6   | 1,9        | 1.1   | 8,0    | 4,8  | 4.2  | Tr.         | 1,1        | 2) 5         | 12,3 | 19,7 |
| s of   |                   | Ξ                              | 4.6  | 7.1   | 2,4        | 1,9   | 5,5    | 10.1 | 10,1 | 2.4         | 4,3        | 23.8         | 19,1 | 28,1 |
| lucta  |                   | =                              | 3.8  | 1,2   | 0,9        | 0.6   | 1,3    | 0.4  |      | 1.4         | 2,9        | 5.4          | Ц.   | 3,1  |
| Proc   |                   | >                              | 4.8  | 5.0   | 6.1        | 1,1   | 0.6    | 3.6  | 6,4  | 7.9         | 5,6        | 11.2         | 5.1  | 6•9  |
| the  |                   | -                              | 10.2 | 10,01 | 13,4       | 19,61 | 13 9   | 8.8  | 12.1 | 13.4        | 8,0        | 24.7         | 6.8  | 26,1 |
| TABLE 2. Compositions of the Products of the Liquid-Phase Oxidation of 3-Caren | of the oxidate, % | polymers                       | 24.4 | 20,3  | 26,7       | 14.0  | 9,5    | 20.6 | 26.4 | 29,1        | 15,2       | 13 4         | 12,4 | 16.3 |
|  |                   | 02-con-<br>taining<br>fraction | 57,5 | 54,3  | 51,1       | 50,7  | 51,5   | 57,1 | 55,0 | 49,5        | 42,5       | 34,6         | 9,3  | 44,7 |
| 2.   | Comp              | hydro<br>car-<br>bons          | 18,1 | 25,4  | 22,2       | 35,3  | 39,0   | 22,3 | 18,6 | 21,4        | 42,3       | 52 0         | 78,3 | 39_0 |
| TABLE  | Ë                 | peri-<br>ment<br>No.           |      | 5     | <i>с</i> о | 4     | ۍ<br>ا | 9    | 7    | œ           | 6          | 10           | Ξ    | 12   |

\*Unidentified components.

(XI)-XIV). The formation of the latter has been observed in the photooxidation of 3-carene [13, 14], the amount of the alcohol (XII) reaching 50%. In the reactions that we investigated, the alcohols (XI)-(XIII) accumulated in small amounts (their total content in the oxidates ranged from 0.5 to 10.3%), which can be explained by the instability of these compounds under the reaction conditions investigated. It is likely that, under the conditions of oxidation, homoallyl rearrangements take place with the opening of the cyclopropane ring (CPR) and the formation of p- and m-menthadienols (XIX and XX), which, in their turn, are converted into the terpineols (XVII and XVIII) and the aromatic alcohols (XV and XVI). The presence of the menthadienols (XIX) and (XX) in the products of the oxidation of 3-carene in the presence of cobalt stearate has been established previously by Baines and Cocker [17]. The oxidation of the allyl methylene groups of ketones (I) and (V) formed the dione (VI), which has been described in [23].

In addition to oxidation, under the reaction conditions compounds (I) and (V) isomerized into the trimethylcycloheptadienones (III) and (IV). This transformation includes two types of tautomerism: keto-enol and valence of the type of norcaradiene-cycloheptatriene.



The addition of oxygen at the double bond of 3-carene led to the formation of  $3,4\alpha$ -epoxycarane (VII) the amount of which ranged from traces to 24%, depending on the reaction conditions. The presence of small amounts of the epoxide (VII) (up to 3.8%) in the products of the catalytic autooxidation of 3-carene has also been reported [17]. During the reaction, the  $3,4\alpha$ -epoxycarane underwent isomerization, which took place with the opening of the oxirane ring and the contraction of the 6-membered ring. As a result, the aldehyde (VIII) with a bicyclo[3.1.0]hexane skeleton was formed. The alcohol (IX) with the same skeleton was a product of the reduction of the aldehyde (VIII) in a hydrogen disproportionation process.

The pathways of the formation of the identified products of the oxidation of 3-carene can be represented by a generalized scheme.

The facts given in Table 2 show that the nature of the catalyst has a substantial effect on the qualitative composition of the oxidate. When cobalt acetate was used in the absence of solvents (experiment 5), both allyl oxidation with the formation of the ketones (I-V) and the diketone (VI) (totaling 49%) and the addition of oxygen at the double bond with the formation of the epoxide (VII) (24%) took place. When oxidation was performed with this catalyst in acetic acid (experiment 2), the predominating process was allyl oxidation, but, in addition to compounds (I-VI) (48.5%), products of secondary transformations were formed - the aromatic alcohols (XV) and (XVI), the menthenols (XVII) and (XVIII), and the menthadienols (XIX) and (XX) (totaling 45.7%). Similar results were obtained on the catalytic oxidation of 3-carene in formic acid (experiment 9), but in this case the amount of the ketones (I-V) fell (21.9%) and there was practically none of the diketone (VI), while the amount of the alcohols (XV-XX) increased (53.4%).

On the oxidation of 3-carene in the absence of solvents and with the addition of a manganese salt to the catalytic system (experiment 1), the process took place in both directions. The main products of allyl oxidation were the ketones (I-V) (29.3%) and the momocyclic alcohols (XV-XX) (38.3%), while the main product of oxidation at the double bond was the bicyclic aldehyde (VIII) (18.5%). Performing the oxidation of 3-carene with the catalytic system in an acid medium (experiments 3 and 4) activated the occurrence of allyl oxidation.

When 3-carene was oxidized with an aqueous solution of NaOH (experiment 10) the amount of oxygen-containing products in the oxidate fell in comparison with the catalytic process. However, at the same time, a high selectivity was observed, as the amounts of allyl oxidation exceeded 90% and the main components were mono- and bicyclic ketones in approximately equal amounts. The addition of cobalt stearate and o-phenanthroline to this system (experiment (12) lowered the amount of bicyclic ketones to 36.1% and increased the yield of monocyclic ketones to 47.8%, with a considerable rise in the total yield of oxygen-containing compounds.



Scheme of the formation of oxygen-containing products in the liquid-phase oxidation of 3-carene.

Thus, the use of different catalytic systems permits the amounts of individual components in the products of oxidation of 3-carene to be regulated.

## EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer in a thin layer, and PMR spectra on a Bruker WM-360 spectrometer in  $CDCl_3$  with HMDS as internal standard. Mass spectra were recorded on a Varian MAT-311 instrument at an energy of the ionizing electrons of 24 eV.

GLC analysis was conducted on a Chrom-4 instrument with a FID in stainless steel capillary columns (0.25 mm  $\times$  50 m) using tricresyl phosphate and squalane as the liquid phases at a thermostat temperature of 105°C and an evaporator temperature of 200°C [25]. The isolation of individual substances by preparative GLC was performed under the conditions described in [26].

The initial 3-carene was isolated from the depinenated turpentine of the Borisov woodchemical factory by fractional distillation in a column with an efficiency of 100 theoretical plates. The experiments were performed on a concentrate containing 99.5-99.8% of the main substance.

The oxidation of 3-carene was performed with molecular oxygen by the procedure of [22]. The hydrocarbons and unchanged 3-carene with bp 55-70°C (10 mm) were distilled off from the autooxidation product, and then the oxygen-containing fraction was distilled, with bp 75-120°C (5 mm). The compositions of the catalyst used, the reaction conditions, and the amounts of oxygen absorbed are given in Table 1. The degrees of conversion of the 3-carene and the yields of the oxygen-containing fractions and their compositions are given in Table 2.

Isolation of the Individual Ketones and Alcohols. In order to separate the ketones, the oxidate was treated with Girard's reagent by the procedure of [27]. The complex compound so obtained was decomposed with acid, and individual ketones were isolated by preparative GLC from the resulting concentrate of carbonyl compounds. Tertiary alcohols were isolated by preparative GLC from the oil freed from carbonyl compounds. Alcohols (XV-XVIII) were isolated from the oxidate of experiment 8, ketones (I) and (II) from the product of experiment 4, ketones (III) and (IV) from the oxidate of experiment 10, and the diketone (VI) from the product of experiment 2.

The epoxide (VII) and the aldehyde (VIII) were isolated by preparative GLC from the products of experiments 5 and 6, respectively.

The physicochemical and spectral properties of compounds (I-VIII) and (XV-XVII) corresponded to those given in the literature [17, 26, 28-32]. Alcohols (IX-XIII), (XIX), and (XX) were identified by the addition of model compounds under the conditions of GLC analysis in capillary columns with liquid phases of different polarities. The model compounds were obtained by independent synthesis using known methods [12, 26, 28].

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