## OXIDATION OF 3-CARENE WITH MERCURIC ACETATE

(UDC 547,599.7)

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A. M. Butlerov Chemical Institute and V. I. Ul'yanov-Lenin Kazan' State University Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 466-475, March, 1965 Original article submitted March 11, 1963

As we have already reported [1], in the autoxidation of 3-carene in presence of lead acetate and in its oxidation with lead tetraacetate one of the reaction products is the dienic (+)-alcohol  $C_{10}H_{16}O$  or its acetate. This alcohol, which is formed also in the oxidation of 3-carene with selenium dioxide (the identity of the alcohols from these reactions was proved by us), was assigned the structure of 3-caren-10-ol by Zacharewicz and co-workers [2]. In our investigations the structure of the dienol has not been established. Continuing our search for ways of obtaining the (+)-alcohol as the main reaction product, we studied the oxidation of 3-carene with mercuric acetate and repeated the experiments of Zacharewicz and co-workers (the results will be reported in the next communication).

In the researches of Treibs [3-6] and Kergomard [7] it was shown that mercuric acetate acts on unsaturated cyclic hydrocarbons in an analogous way to lead tetraacetate with the difference that in this reaction only the allyl replacement of hydrogen atoms of methylene groups by the acetoxy group occurs, i.e., acetates of  $\alpha$ , $\beta$ -unsaturated alcohols are formed, and the formation of diacetates does not occur. It could be expected that the oxidation of 3-carene with mercuric acetate would lead to the acetate of the same dienic (+)-alcohol as that which we isolated from the products of the autoxidation reaction and of oxidation with lead tetraacetate.

It was in fact found that the main products of the oxidation of 3-carene with mercuric acetate was the dienic (+)-alcohol which we have already described. In preparative respects this reaction was found to be more convenient, for in the first place the yield of the acetate of the (+)-alcohol was higher than in oxidation with lead tetraacetate, as studied by us earlier, and in the second place the simpler course of the reaction makes it possible to isolate the required acetate from the reaction products with relative ease and in a purer state. This last fact is evident when



Fig. 1. Ultraviolet spectra: 1) (+)-alcohol from the 3,5-dinitrobenzoate; 2) acetate of (+)-alcohol; 3) (+)-alcohol from the acetate; 4) product of the oxidation of the (+)-alcohol; 5) thymol; 6) p-cymene.





Fig. 2. Infrared spectrum of the (+)-alcohol from its 3,5-dinitrobenzoate.

Fig. 3. Infrared spectrum of the product of the oxidation of (+)-alcohol.

we compare the constants of hydrolysis products from individual fractions of the acetate of the (+)-alcohol and of the (+)-alcohol from the autoxidation of 3-carene in presence of MnO<sub>2</sub>, as purified via the 3,5-dinitrobenzoate (ultraviolet spectrum, Fig. 1, Curve 1; infrared spectrum, Fig. 2). By the oxidative acetylation of 3-carene with mercuric acetate we obtained the acetate of the (+)-alcohol and also the (+)-alcohol itself in the amounts and state of purity necessary for the establishment of their structures.

Raman spectrum data, which point to the presence of a conjugated system of double bonds in the molecules of the acetate and the (+)-alcohol, were confirmed in the present work by chemical methods. It was found that both the acetate and the (+)-alcohol readily undergo diene condensation: the acetate gives an adduct with maleic anhydride and with 1,4-naphthoquinone, and the alcohol gives an adduct with 1,4-naphthoquinone. To establish the positions of the double bonds in the ring we used the method of converting the 1,4-naphthoquinone adducts into anthraquinone derivatives. By the dehydrogenation of the 1,4-naphthoquinone adducts of the acetate and the (+)alcohol and then heating the dehydrogenation products to eliminate the endo bridge we obtained 2-methylanthraquinone. The formatio of 2-methylanthraquinone in this series of reactions is only possible if an isoprene grouping is present in the acetate and (+)-alcohol molecules. However, on the basis of these data alone both a cyclohexadiene and a cycloheptadiene structure could be proposed for the acetate and the (+)-alcohol. The choice between these can be made from the ultraviolet spectra of the acetate and the (+)-alcohol, which contain absorption bands with  $\lambda_{\text{max}}$  262.5 m $\mu$  (log  $\varepsilon$  3.55) (Fig. 1, Curves 2 and 3) characteristic for cyclohexadiene systems of the p-mentha-1,5-diene,  $\alpha$ -zingiberene, and other types [8]. For an alcohol of the cycloheptadiene type-eucarveol -absorption in the ultraviolet with  $\lambda_{max}$  248 m $\mu$  (log  $\epsilon$  3.87) is characteristic [9]. Also, on dehydration with iodine the (+)-alcohol gave p-cymene (ultraviolet spectrum, Fig. 1, Curve 6), which was identified by oxidation to terephthalic acid and the conversion of the latter into dimethyl terephthalate. Hence, the acetate and the (+)alcohol are compounds of the p-menthadiene series.

We have already stated that the (+)-alcohol or its acetate is formed as a result of the autoxidation of 3-carene in presence of lead acetate and in its oxidation with selenium dioxide, lead tetraacetate, and mercuric acetate. It is known that in these reactions the molecule of the unsaturated cyclic hydrocarbon is attacked at the CH<sub>3</sub> and CH<sub>2</sub> groups in the  $\alpha$ -position relative to the double bond and that the reaction products are  $\alpha$ ,  $\beta$ -unsaturated alcohols or their acetates. In this case a possible structure of the (+)-alcohol must be that of p-mentha-1,5-dien-3-ol.

For the oxidation of unsaturated hydrocarbons with lead tetraacetate and with mercuric acetate a mechanism has been proposed [7, 10-12] whose first stage consists in the addition of an oxidant molecule at the double bond, which is followed by the elimination of a molecule of acetic acid and of lead or mercury acetate from the addition product. The formation of p-mentha-1,5-dien-3-ol in the reaction of 3-carene with mercuric acetate may be

represented as proceeding by a scheme analogous to that proposed by Whitham [10] for the oxidation of  $\alpha$ -pinene with lead tetraacetate:



In this it is assumed that the primary reaction product is 4-caren-3-ol acetate, which is unstable in presence of acetic acid and is isomerized into 3-caren-5-ol acetate; the latter is isomerized into p-mentha-1,5-dien-3-ol.

Final confirmation of the structure of p-mentha-1,5-dien-3-ol assigned to the (+)-alcohol would be provided by the formation of thymol in its oxidation with chromic anhydride. The oxidation product was indeed found to be a substance of composition  $C_{10}H_{14}O$  containing an OH group, but it differed from thymol in the melting points of its 3,5-dinitrobenzoate (193-195.5°) and 1-naphthylurethan (140.5-141.5°). Its infrared spectrum (Fig. 3) and ultraviolet spectrum (Fig. 1, Curve 4) were also not identical with the corresponding spectra of thymol. The infrared spectrum of the oxidation product contains an intense band at 1519 cm<sup>-1</sup>, but there are no bands at 1575 and 1618 cm<sup>-1</sup>, which are found in the infrared spectrum of thymol (Fig. 4). The ultraviolet spectrum of thymol (Fig. 1, Curve 5) has  $\lambda_{max}$  220 m $\mu$  (log  $\varepsilon$  3.77) and  $\lambda_{max}$  277.5 m $\mu$  (log  $\varepsilon$  3.37). The absorption band of the oxidation product has four maxima: 220 m $\mu$  (log  $\varepsilon$  3.86), 232.5 m $\mu$  (log  $\varepsilon$  3.24), 265 m $\mu$  (log  $\varepsilon$  2.58), 272.5 m $\mu$ (log  $\varepsilon$  2.56).

Convincing information on the structure of the alcohol was obtained from the PMR spectra (Fig. 5). The chemical shift ( $\tau$ ) was determined relative to tetramethylsilane (taken as 10). Benzene was used for the calibration of the spectrum. The spectrum contained: two peaks ( $\tau$  4.22 and 4.65) close to 3H in area and corresponding to the grouping CH= (in cyclohexadiene  $\tau$  = 4.22 [13, p. 290]), a peak due to a hydroxyl proton at  $\tau$  = 6.20 (1H), and a peak at  $\tau$  = 7.72 (about 3H), close to that of the grouping CH<sub>2</sub>-CH= [13, p. 288] in 1,3-cyclohexadiene. A peak at  $\tau$  = 8.22 (4H) corresponds to a methyl group at a double bond.<sup>\*</sup> There is a sharp peak at  $\tau$  = 8.80 (6H). The low value of the chemical shift and the absence of a doublet indicate that two methyl groups are on a carbon attached



<sup>\*</sup>One proton of a -CH group probably contributes to this peak.

In this case the oxidation product should be p-cymen-8-ol. We confirmed this supposition by comparing the infrared spectrum (Fig. 6) and the PMR spectrum (Fig. 7) of the oxidation product with those of p-cymen-8-ol. The PMR spectrum contains a peak at  $\tau = 2.85$  (4H) corresponding to the protons of the benzene ring and a peak at  $\tau$  = 7.85 (3H) close to that of the CH<sub>3</sub> group of toluene substituted in the para position [15]. The values of  $\tau$  = 5.57 of the hydroxy group (1H) and  $\tau$  = 8.58 of the (CH<sub>3</sub>)<sub>2</sub>C grouping (6H) are lower than in the spectrum in Fig. 5, which

indicates an approach toward a benzene nucleus. The (+)-alcohol must therefore have the structures of p-mentha-1,5-dien-8-ol. To prove this conclusively we decided to establish the nature of the product eliminated when the dehydrogenated 1,4-naphthoquinone adduct of the (+)-alcohol is heated in the experiment on the formation of 2-2-methylanthraquinone. This series of transformations may be represented schematically as follows:

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The dehydrogenated 1,4-naphthoquinone adduct of p-mentha-1,5-dien-8-ol should split into 2-methylanthraquinone and 2-methyl-3-buten-2-ol (infrared spectrum, Fig. 8). The second product of the cleavage was indeed found to be 2-methyl-3-buten-2-ol [16] (infrared spectrum, Fig. 9).

The formation of p-mentha-1,5-dien-8-ol in the autoxidation of 3-carene by a free-radical mechanism may be explained by the rearrangement of the radical (I), the product of the attack of the 3-carene molecule at the 5-CH<sub>2</sub> group.



Fig. 6. Infrared spectrum of p-cymen-8-ol.

An analogous case of rearrangement in a radical of the terpene series has been described earlier [17] in a study of the addition of  $CCl_4$  to  $\beta$ -pinene in presence of a peroxide catalyst. However, the mechanism of the formation of p-mentha-1,5-dien-8-ol acetate in the oxidative acetylation of 3-carene with lead tetraacetate and mercuric ace-

In the preceding communication [1] we reported that, on oxidation with the pyridine complex of  $CrO_3$ , the (+)alcohol gives a ketone whose 2,4-dinitrophenylhydrazone



Fig. 7. PMR spectrum of the product of the oxidation of the (+)-alcohol.



Fig. 8. Infrared spectrum of 2-methyl-3-buten-2-one.



Fig. 9. Infrared spectrum of 2-methyl-3-buten-2-one from the 1,4-naphthoquinone adduct of the (+)-alcohol.

has the same melting point as that of 3-caren-10-al [2]. Such contradictions in data on the nature of the product of the oxidation of the (+)-alcohol may be explained on the view that the (+)-alcohol used previously for chromic anhydride oxidation was not homogeneous. The alcohol was prepared by the hydrolysis of the acetate isolated by the fractionation of the products of the oxidation of 3-carene with lead tetraacetate. The hydrolysis product was probably a mixture of alcohols, one of which gave a ketone on oxidation with the pyridine complex of  $CrO_3$ . Also, the possibility cannot be excluded that this ketone was present already in the product of the hydrolysis of the acetate, as was observed for 3,6,6-trimethyl-2,4-cycloheptadien-1-one [1]. However, in the oxidation of the (+)-alcohol obtained by autoxidation in presence of  $MnO_2$  and purified via the 3,5-dinitrobenzoate and that obtained from the products of the hydrolysis of the acetate arising in the reaction of 3-carene with mercuric acetate, we always obtained p-cymen-8-ol.

Apart from the acetate of p-mentha-1,5-dien-8-ol, in the oxidation of 3-carene with mercuric acetate the acetate of another alcohol was formed, and in view of the small amount obtained this was not investigated in detail. The alcohol was found to be a (-)-dienol  $C_{10}H_{16}O$ containing a conjugated system of double bonds. Its ultraviolet spectrum had  $\lambda_{\max}$  230 m $\mu$  (log  $\varepsilon$  4.14), which in intensity is analogous to those of  $\beta$ -phellandrene and p-mentha-3,8(9)-diene [8].

## EXPERIMENTAL

The infrared spectra were run on an IKS-14 double-beam spectrometer and on a Hilger H-800 spectrometer with an NaCl prism. The ultraviolet absorption spectra were measured with an SF-4 spectrophotometer; solvent methanol, concentration of solutions about 0.01 M. The NMR spectra were run on a high-resolution YaMR-KGU-1 NMR spectrometer [18],  $v_0 = 24.458$  MHz, resolving power 5  $\cdot$  10<sup>-8</sup>; recording without the use of electric shims and without superstandardization of the magnetic flux; with rotation of sample; diameter of ampoules 2 mm, amount of substance about 0.1 ml, room temperature.

Oxidation of 3-carene with mercuric acetate. A mixture of 65 g of 3-carene and 150 g of mercuric acetate was heated in an oil bath for

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Fraction	B.p., °C (p, mm)	Wt., g	n <mark>20</mark>	d <b>20</b>	$\alpha_{\rm D}^0$
I II IV VI VII VII VIII IX XI XII XIII XIV XV XVI	$\begin{array}{c} 59-60 (17)\\ 60-62 (17)\\ 62-71 (17)\\ 71-77 (17)\\ 77-78 (17)\\ 78 (17)\\ 78 (17)\\ 78 (17)\\ 71-100 (9)\\ 100-101 (9)\\ 101-103 (9)\\ 103 (9$	5,7 5,1 1,95 1,4 1,6 9,50 4,50 2 3,2 4,4 7,95 3,65 9,18 7,57 4,65 6,0	$\begin{array}{c}\\ 1,4790\\ 1,5010\\ 1,5245\\ 1,5335\\ 1,5355\\ 1,5049\\ 1,4815\\ 1,4794\\ 1,4794\\ 1,4794\\ 1,4795\\ 1,4796\\ 1,4810\\ 1,4810\\ 1,4820\\ 1,4820\\ 1,4850\end{array}$	  0,9055 0,9048 0,9592 0,9815 0,9797 0,9800 0,9795 0,9786 0,9797 0,9783 0,9797 0,9783 0,9809 0,9815	+ 15,85 + 15,65 + 14,35 + 7,35 + 3,0 + 0,65 0 + 39,35 + 106,0 + 118,35 + 122,65 + 120,0 + 118,35 + 122,65 + 120,0 + 114,0 + 105,0 0 30 35
XVIII XIX	103 (9) 103104 (9) 104 (9) Residue	4,3 3,7 6,3	1,490) 1,4910	0,9969 1,007	+ 33,0 + 4,65

3.5-4 h at 142-155°. Acetic acid distilled off, and mercury was precipitated. Mercury was filtered off, and the reaction mixture was washed with water, sodium carbonate solution, and again water and was dried with sodium sulfate. In all, we oxidized 300 g of 3-carene with 695 g of mercuric acetate. By fractionation of the reaction mixture we obtained 139.1 of unoxidized 3-carene, 90.5 g of reaction products as distillate, and 65.28 g of resinous residue. The reaction products were fractionated through a column of 17-plate efficiency. The results are summarized in the table.

Maleic anhydride adduct of the substance of fraction X. A mixture of 1 g of the acetate and 0.5 g of maleic anhydride was heated in a sealed tube in a water bath, and we obtained 0.8 g of the adduct (yield 53.3%); m.p. 145-146.2° (after three crystallizations from a mixture of benzene and petroleum ether);  $[\alpha]_D$  + 29.15° (c 1,716; CHCl<sub>3</sub>). Found: C 65.89; H 7.01%. C<sub>16</sub>H<sub>20</sub>O<sub>5</sub>. Calculated: C 65.74; H 6.90%.

1,4-Naphthoquinone adduct of the acetate in fraction X. A mixture of 1.7 g of the acetate of the (+)-alcohol, 1.4 g of 1,4-naphthoquinone, and 2.5 ml of ethanol was heated in a sealed tube in a water bath for four hours. We obtained 1 g (32.4%) of the adduct, which after crystallization from petroleum ether had m.p. 69.5-71°. Found: C 75.05; H 6.91%. C<sub>29</sub>H<sub>24</sub>O<sub>4</sub>. Calculated: C 74.97; H 6.86%.

<u>Dehydrogenation of the adduct of m.p. 69.5-71</u>°. Four drops of alcoholic potassium hydroxide was added to a solution of 1 g of the adduct in 8 ml of absolute alcohol, which then became dark red; the solution was heated in a water bath, and air was blown through for two hours. The color of the solution changed to yellowish red. After the removal of ethanol the dehydrogenation product formed a noncrystallizing oil.

Preparation of 2-methylanthraquinone from the dehydrogenated adduct. To remove the endo bridge from the molecule of the dehydrogenated adduct, the noncrystallizing oil was heated in a bath of Wood's metal at 165° for one hour. The solid substance formed had m.p. 174-174.5° after two crystallizations from petroleum ether. A mixture with the 2-methylanthraquinone (m.p. 173-174°) prepared analogously from the 1,4-naphthoquinone adduct of isoprene melted without depression.

<u>Hydrolysis of fraction XII.</u> 7.7 g of the substance was heated in 1.5% aqueous-alcoholic NaOH for four hours. The reaction mixture was poured into water and extracted with ether. The ether extract was washed with water and dried with Na<sub>2</sub>SO<sub>4</sub>. After the removal of ether the residue was vacuum-distilled. We obtained 5.4 g (88.8%) of product; b.p. 70-71° (4 mm);  $n_D^{20}$  1.4987;  $d_4^{20}$  0.9545;  $[\alpha]_D$  + 141.2°. Found MR 46.73. C<sub>10</sub>H<sub>16</sub>OF<sub>2</sub>. Calculated MR 46.77.

Raman spectrum ( $\Delta\nu$ , cm<sup>-1</sup>): 149 (2), 227 (1), 266 (1), 307 (1), 343 (0), 426 (1), 462 (1), 495 (1), 521 (0), 535 (0), 580 (2), 603 (2), 686 (1), 733 (0), 775 (4), 829 (1), 845 (1), 926 (2), 952 (1), 1111 (1), 1130 (1), 1176 (5), 1206 (4), 1255 (2), 1405 (3), 1436 (4), 1450 (4), 1592 (10 w), 1635 (8), 1656 (2), 2818 (3), 2860 (3), 2883 (3), 2913 (10), 2936 (10), 2974 (10), 3021 (5), 3035 (5).

The 3,5-dinitrobenzoate of the hydrolysis product had m.p. 94-96°. A mixture with the 3,5-dinitrobenzoate of the (+)-alcohol obtained in the autoxidation of 3-carene melted without depression. The 1-naphthylurethan, prepared from 0.2 g of the hydrolysis product, 0.22 g of 1-naphthyl isocyanate, and two drops of pyridine, had m.p. 104.5-105.5° after three crystallizations from petroleum ether. Found: C 78.28; H 7.43%.  $C_{21}H_{23}NO_2$ . Calculated: C 78.47; H 7.21%.

 $\frac{1,4-\text{Naphthoquinone adduct of the (+)-alcohol of b.p. 70-71^{\circ} (4 \text{ mm})}{\text{g of 1,4-naphthoquinone, and 1.5 ml of ethanol was heated for seven hours in a water bath. By repeated extraction with boiling petroleum ether (70-100°) and boiling the solutions with charcoal we obtained 0.77 g of long needles, m.p. 125-126°. Found: C 77.32; H 7.11%. C<sub>20</sub>H<sub>22</sub>O<sub>3</sub>. Calculated: C 77.38; H 7.15%.$ 

Preparation of the 3,5-dinitrobenzoate of the (+)-alcohol from the products of the oxidation of 3-carene with oxygen in presence of  $MnO_2$ . 26.85 g of the substance with b.p. 85-92° (5 mm) and  $[\alpha]_D$  + 72.66° was treated with 41.57 g of 3,5-dinitrobenzoyl chloride in 500 ml of benzene, after which 35 ml of pyridine was added to the reaction mixture. After the usual treatment we obtained 4.2 g of the 3,5-dinitrobenzoate, m.p. 90-92°.

<u>Hydrolysis of the 3,5-dinitrobenzoate of m.p. 90-92</u>°. Hydrolysis of 4.2 g of the 3,5-dinitrobenzoate of the (+)-alcohol with 1% aqueous-alcoholic NaOH gave 1.63 g of a substance of b.p. 71-72° (4 mm);  $n_D^{20}$  1.4980;  $d_4^{20}$  0.9497;  $[\alpha]_D$  + 163.21°. Found MR 46.91.  $C_{10}H_{16}OF_2$ . Calculated MR 46.77.

Dehydration of the product of the hydrolysis of fraction XII. A mixture of 2 g of the alcohol and 0.02 g of doubly sublimed iodine was heated under reflux in an atmosphere of nitrogen. At 90° the rapid liberation of water

began. The reaction mixture was diluted with ether, washed with 2 N NaOH and water, and dried with Na<sub>2</sub>SO<sub>4</sub>. We obtained 1.32 g of a hydrocarbon (yield 75%); b.p. 69-72° (19 mm);  $n_D^{20}$  1.4919;  $d_4^{20}$  1.8612. Found MR 44.95. C<sub>10</sub>H<sub>14</sub>F<sub>3</sub>. Calculated MR 44.78.

Oxidation of the product of b.p.69-72° (19 mm) with chromic acid. A cooled solution of 5 ml of sulfuric acid in 10 ml of water was added to a solution of 5 g of  $CrO_3$  in 15 ml of 60% acetic acid, and to this mixture 0.5 g of the hydrocarbon of b.p. 69-72° (19 mm) was added cautiously. The reaction mixture was heated in a water bath for about two hours and then poured into water. The white precipitate of acid which formed was filtered off.

Preparation of dimethyl terephthalate. Hydrogen chloride was passed for one hour through a methanolic solution of the acid obtained by the oxidation of the dehydration product. The solution was then vacuum-evaporated at room temperature. The resulting precipitate had m.p. 138-140° after recrystallization from water. A mixture with dimethyl terephthalate (m.p. 140-141°) melted without depression.

Hydrolysis of the substance of fraction XIV. By the hydrolysis of 9.1 g of the substance with 1.5% aqueous alcoholic NaOH we obtained 6.4 g (89.8%) of product; b.p. 66-67° (2.5 mm);  $n_D^{20}$  1.4994;  $d_4^{20}$  0.9548;  $[\alpha]_D$  + 138.57°.

Oxidation of the product of b.p. 66-67° (2.5 mm) with the pyridine complex of  $\text{CrO}_3$ . The complex was prepared from 4.8 g of  $\text{CrO}_3$  and 48 ml of pyridine. A solution of 2 g of the substance in 20 ml of dry pyridine was added dropwise to the complex, diluted with 30 ml of pyridine. The reaction mixture was left overnight at room temperature and then diluted with water and extracted with a mixture of benzene and ether. We obtained 1.15 g of of the oxidation product (yield 58%); b.p. 65-66.5° (2 mm);  $n_D^{20}$  1.5150;  $d_4^{20}$  0.9736;  $\alpha_D - 1^6$ . Found MR 46.46.  $C_{10}H_{14}OF_3$ . Calculated MR 46.30.

<u>The 3,5-dinitrobenzoate</u> of the oxidation product melted in a somewhat unusual way: at 102-104° the substance in the capillary diminished in volume and melted slightly, and it then rapidly solidified again and melted at 193-195.5°. Found: C 59.31; H 4.86%.  $C_{17}H_{16}O_6N_2$ . Calculated: C 59.30; H 4.68%.

The 1-naphthylurethan had m.p. 140.5-141.5°. Found: C 79.00; H 6.62%. C<sub>21</sub>H<sub>21</sub>NO<sub>2</sub>. Calculated: C 78.97; H 6.63%.

<u>p-Cymen-8-ol</u> was prepared from p-tolyImagnesium bromide and acetone [19] by the procedure described for the synthesis of  $\alpha$ -methylbenzhydrol [20]; b.p. 102-103° (13 mm);  $n_D^{20}$  1.5189;  $d_4^{20}$  0.9714. The 3,5-dinitrobenzoate had exactly the same melting point as the 3,5-dinitrobenzoate of the product of the oxidation of the (+)-alcohol. A mixture of them melted at 193-195° (at 102-104° a brief partial melting occurred).

Preparation of 2-methyl-3-buten-2-ol from the 1,4-naphthoquinone adduct. The 1,4-naphthoquinone adduct of the (+)-alcohol was prepared from 3 g of the (+)-alcohol and 3.2 g of 1,4-naphthoquinone in 2.5 ml of ethanol. Without preliminary isolation and purification the adduct was dehydrogenated by passing air through its boiling alcoholic solution in presence of a few drops of alcoholic KOH. Ethanol was driven off, and traces of it were removed by heating the reaction flask under a vacuum of 4 mm.

The dehydrogenation product—a reddish-brown glassy mass—was heated in a bath of Wood's metal at 210°, and 0.85 g of a substance with  $n_D^{20}$  1.4170 came over; for 2-methyl-3-buten-2-ol  $n_D^{20}$  1.4140 [13]. When treated with 3,5-dinitrobenzoyl chloride the elimination product gave two 3,5-dinitrobenzoates: 1) m.p. 93-94° and 2) m.p. 103-105°. The 3,5-dinitrobenzoate of m.p. 93-94° was found to be the ethanol derivative (proved by a mix-ture test).

To identify the 3,5-dinitrobenzoate of m.p.  $103-105^{\circ}$  we prepared the 3,5-dinitrobenzoate of 2-methyl-3buten-2-ol, m.p. 106-107° (b.p. 94-95°;  $n_D^{20}$  1.4160,  $d_4^{20}$  0.8241). A mixture of the two substances melted without depression.

Hydrolysis of fraction XIX. 3.7 g of the product was heated in 100 ml of 1% alcoholic NaOH for four hours in a boiling water bath. The reaction mixture was treated in the usual way, and we obtained 1.4 g (50%) of product; b.p. 64-65° (1.5 mm),  $n_D^{20}$  1.5140;  $d_4^{20}$  0.9696;  $\alpha_D$ -10.2°. Found MR 47.20.  $C_{10}H_{16}OF_2$ . Calculated MR 46.77. 3,5-Dinitrobenzoate, m.p. 121-123°. Found: C 58.89; H 5.29%.  $C_{17}H_{18}N_2O_6$ . Calculated: C 58.95; H 5.24%.

\* As in original-Publisher's note.

## SUMMARY

The oxidation of 3-carene with mercuric acetate was studied. The oxidative acetylation of 3-carene with mercuric acetate leads to a less complex mixture of products than oxidation with lead tetraacetate. The main products are p-mentha-1,5-dien-8-ol and, in smaller amount, p-isopropenyltoluene.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.