OXIDATION OF 3- AND 4-CARENES WITH MERCURIC ACETATE IN ACETIC ACID

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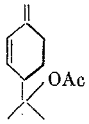
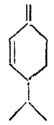
Previously we have studied the acetylative oxidation of 3-carene with mercuric acetate [1] under the conditions developed by Treibs [2, 3]. The products of this reaction were p-methylisopropenylbenzene (19%), p-mentha-1,5-dien-8-ol acetate (69%), and a small amount of the acetate of the alcohol containing the carbon skeleton of β-phellandrene (12%). The conclusive structure of this acetate was not established due to its small amount. Recently some data appeared on the mechanism of the reaction for the oxidation of olefins with mercuric acetate in acetic acid and, in particular, on the mechanism for the formation of the acetates of allylic alcohols [4-7]. According to this mechanism, allylic mercuriacetates are regarded as being the intermediate products, the acetolysis of which can be accompanied by allylic rearrangement and leads to the formation of a mixture of acetates. In view of this it was interesting to study the oxidation of 3-carene with mercuric acetate under analogous conditions.

When 3-carene is oxidized with mercuric acetate in acetic acid, with gradual increase in the temperature from room temperature up to 86° there is observed the initial appearance of a precipitate of mercurous acetate and its subsequent disappearance with the deposition of metallic mercury. The reaction products proved to be p-methylisopropenylbenzene (I), p-mentha-1,5-dien-8-ol acetate (II) and the acetate of the alcohol with the carbon skeleton of β-phellandrene, i.e., the same compound that is obtained when the oxidation is run at 140° without a solvent [1].

We assigned the structure of p-mentha-1(7),5-dien-8-ol acetate (III) to the acetate containing the β-phellandrene carbon skeleton, basing ourselves on the following physical and chemical data. In the IR spectrum of the corresponding alcohol, obtained in the pure state from the 3,5-dinitrobenzoate with mp 129-131°, is present an absorption band that is characteristic for a system of conjugated double bonds (1600 cm^{-1}), in which connection one of the double bonds is an unsymmetrically disubstituted double bond ($\nu_{C=CH_2}$ 1640, ν_{C-H} 3080, δ_{C-H} 890 cm^{-1}), while the second is a symmetrically disubstituted double bond ($\nu_{>C=C<}$ 1660, ν_{C-H} 3030, δ_{C-H} 820 cm^{-1}). In the spectrum are also present the absorption bands of a tertiary OH group (ν_{C-O} 1135, 1160, ν_{OH} cm^{-1}). The position of the absorption maximum in the UV spectrum (λ_{max} 230 nm, log ε 4.14) of the alcohol is characteristic for either the β-phellandrene (IV) or the p-mentha-4,8(9)-diene (V) carbon system


(III)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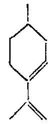
(V)

In the NMR spectrum of the alcohol are present the following chemical shifts (δ, ppm): 1.17 (singlet, 6H $(CH_3)_2\underset{\substack{|\\ O-}}{C}-$); 4.55 (2H, $C=CH_2$); 5.89 (2H, $CH=CH$); 3.35 (1H, OH); 2.13-1.6 (multiplet, 5H, $2CH_2$ groups). As a result, the NMR spectrum of the alcohol is in agreement with the structure of (III). As confirmation of the (III) structure for the dienol is the formation of α-terpineol when it is reduced with Na in ethanol.

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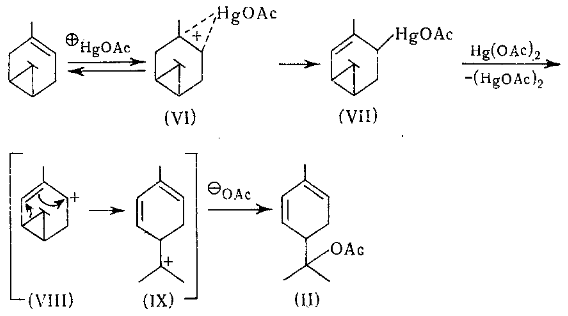
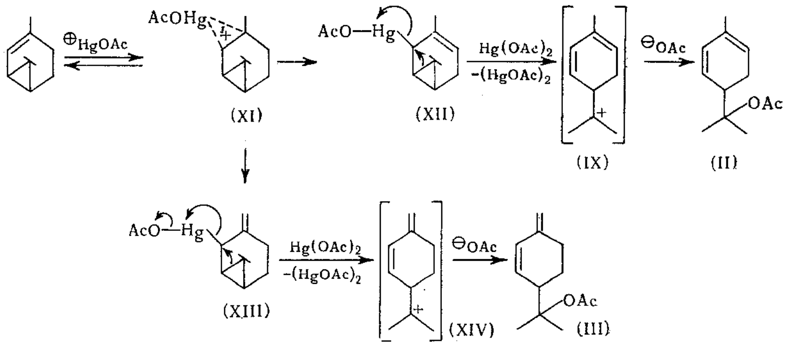
The formation of mercurous acetate during the course of the oxidation reaction, which is reduced to metallic mercury when the temperature is raised, testifies to its oxidative action, which was already mentioned in [3]. The oxidation of 3-carene with mercuric acetate in acetic acid at 23° should exclude the involvement of mercurous acetate in the reaction as an oxidizing agent, which was observed experimentally: mercurous acetate under these conditions is not reduced to metallic mercury to any noticeable degree. Here the same acetates of dienols (II) and (III) and the ketone ($\nu_{C=O}$ 1660 cm^{-1}) were formed, which were not investigated any closer. In addition, the formation of an organomercury compound was observed, which was isolated as a solid and had the composition $C_{18}H_{26}O_8Hg_3$. The IR spectrum of compound (XV) disclosed the presence of an ionized carboxyl group (1320, 1590, 1630 cm^{-1}) and an ester acetate group ($\nu_{C=O}$ 1725, ν_{C-O} 1260, 1025, 1050 cm^{-1}). The treatment of compound (XV) with NaCl gave a product of composition $C_{12}H_{17}O_2Cl_3Hg_3$ (XVI). From this it follows that (XV) contains three acetoxyl groups, which was also corroborated by the IR spectrum of compound (XVI), in which absorption bands, corresponding to the COO^- group, were absent, and the absorption bands of an ester acetate group were retained. Compound (XV) proved to be stable toward such reducing agents as Zn dust and Na amalgam. When treated with $NaBH_4$ in aqueous tetrahydrofuran it gave the partial hydrogenolysis product.

Compound (XV) was not studied any closer. It is probably formed as the result of the action of Hg · $(OAc)_2$ on the intermediate allylic mercuriacetate (VII). An analogous compound is evidently also formed during oxidation by mercuric acetate when the temperature is gradually raised from 19 up to 86°, as is evidenced by an insufficiency in the amount of liberated metallic mercury, constituting 19%. As was shown by special experiment, the oxidation of 3-carene with mercurous acetate at 90° leads to the same products as does the oxidation with mercuric acetate: p-methylisopropenylbenzene and acetates (II) and (III). Organomercury compounds were not isolated in this case. The formation of acetate (II) in the reaction of 3-carene with mercuric acetate is well explained by the mechanism depicted in Scheme 1 [8], and is in agreement with the mechanism proposed in [4] for the acetylative oxidation of olefins with $Hg(OAc)_2$ [4].



Scheme 1

Acetate (II) is the acetolysis product of the allylic mercuriacetate (VII). As regards acetate (III), for its formation by an analogous scheme it is necessary to form mercuriacetate (XIII) during the reaction process; the latter can be depicted by starting with 4-carene, and this, in turn, makes it necessary to assume isomerization under the reaction conditions when 3-carene is oxidized to 4-carene. The possibility of forming acetate (III) in this way was easily checked by effecting the oxidation of 4-carene with mercuric acetate. In this connection, according to Scheme 2, the formation of acetate (II) and acetate (III) could also be expected as acetolysis products of the allylic carenylmercury acetates (XII) and (XIII), which in both cases can proceed with a rearrangement of the allylic type, involving the cyclopropane ring.



Scheme 2

TABLE 1

Fraction	bp, °C (p, mm Hg)	Wt., g	n_D^{20}	α_D^0	Fraction	bp, °C (p, mm Hg)	Wt., g	n_D^{20}	α_D^0
I	До 54 (13)	0,5			XVI	95 (6)	2,63	1,4800	+114
II	54—58 (13)	1,4	1,4720	+14,5	XVII	95 (6)	0,99	1,4805	+118
III	58 (13)	7	1,4725	+15,5	XVIII	95 (6)	2,3	1,4802	+116,83
IV	58 (13)	4,89	1,4725	+15,1	XIX	95 (6)	2,1	1,4802	+113
V	60 (13)	1,3	1,4730	+14,5	XX	93,5—98 (6)	1,6	1,4802	+112
VI	61—72 (13)	1,6	1,4770	+12,3	XXI	98 (6)	2,1	1,4802	+112,5
VII	72 (13)	2,25	1,5295	+0,38	XXII	99,5 (6)	1,49	1,4810	+106,6
VIII	73 (13)	1,96	1,5245	+0,16	XXIII	99,5 (6)	2,54	1,4810	+106
IX	91 (6)	1,8	1,5090	+41,6	XXIV	99,5 (6)	3	1,4820	+99
X	95 (6)	1,8	1,4944	+100,5	XXV	99,5 (6)	2,05	1,4828	+84
XI	95 (6)	1,57	1,4830	+106	XXVI	96 (6)	1,25	1,4839	+73,3
XII	95 (6)	1,5	1,4815	+114	XXVII	96 (6)	0,9	1,4850	+18,5
XIII	95 (6)	1,8			XXVIII	98 (6)	1,35	1,4859	+18,5
XIV	95 (6)	1,6	1,4810		XXIX	98 (6)	1,57	1,4845	+12,5
XV	95 (6)	1,6	1,4310	+114,15	XXX	98 (6)	1,6	1,4825	+1

Actually, we identified (II) and (III) in the oxidation products of 4-carene. The same as in the oxidation of 3-carene, an organomercury compound of the same composition $C_{18}H_{26}O_8Hg_3$ was also isolated in this case. Unfortunately, we were unable to obtain the allylic mercuriacetates $C_{12}H_{18}O_2Hg$ from either 3-carene or 4-carene. For this reason it was impossible for us to accomplish the step of their acetolysis and study the postulated carene—p-menthadiene rearrangements.

EXPERIMENTAL METHOD

The melting points were determined on a Kofler block. The IR spectra were taken on a UR-10 instrument. Analysis by gas–liquid chromatography (GLC) was run on a "Khrom-2" chromatograph, using nitrogen as the carrier gas, firebrick as the solid support, 10% poly(ethylene glycol adipate) as the stationary phase, and a temperature of 140-144°.

Oxidation of 3-Carene with Mercuric Acetate at 19-86°. To a suspension of 100 g of $Hg(OAc)_2$ in 220 ml of CH_3COOH at room temperature was added 46.5 g of 3-carene in drops; here a rise in the temperature from 19 to 32° was observed and also a change in the appearance of the precipitate. After stirring for 2 h at room temperature the reaction mixture was heated up to 86° and kept at this temperature for 1 h. The deposition of metallic mercury was observed (53 g). The solution was poured into water, extracted with ether, and the ether extract was washed in succession with water, $NaHCO_3$ solution and water, and then dried over Na_2SO_4. The ether was distilled off. The residue (46.4 g) was distilled through a fractionating column. A total of 139.5 g of 3-carene was oxidized, employing 300 g of $Hg(OAc)_2$. The liberated metallic Hg represented 81% of theory. The results of subjecting 65 g of the acetylation products to fractional distillation are summarized in Table 1.

The IR spectra and GLC analysis disclosed that fractions X-XXV contain predominantly acetate (II) (the adduct with maleic anhydride had mp 144-146°), while beginning with fraction XXVI the amount of acetate (III) increased noticeably; in the products of fractions XXVIII-XXX it was now present in a predominant amount. Fractions VII-IX contain p-methylisopropenylbenzene (I), which was shown by preparing the dimethyl ester of terephthalic acid with mp 139-140°.

p-Mentha-1(7),5-dien-8-ol. Fractions XXVII-XXX (5.3 g) were saponified with alcoholic caustic solution. The saponification product (3 g, bp 100° (12 mm), α_D +3°] gave the 3,5-dinitrobenzoate with mp 129-131°. The mixed melting point with the analogous derivative of the alcohol with a β-phellandrene carbon skeleton [1] was not depressed. The saponification of the 3,5-dinitrobenzoate with mp 129-131° gave the alcohol with bp 74° (4.5 mm); n_D^{20} 1.5132; d_4^{20} 0.9703; α_D −3.2°; mp 38-41.5°.

Infrared spectrum: 820, 880, 930, 955, 1135, 1160, 1210, 1370, 1380, 1440, 1455, 1470, 1600, 1640, 1660, 3030, 3080, 3400 cm^{-1}.

Reduction of p-Mentha-1(7),5-dien-8-ol with Sodium in Ethanol. To a solution of 0.35 g of the alcohol in 30 ml of absolute ethanol, heated up to the boil, were added small pieces of sodium (0.2 g). The usual workup of the reaction mixture gave the reduction product (0.15 g, n_D^{20} 1.4889), which, based on the GLC data, contained 25% of the starting alcohol and 75% of an alcohol that had the same retention time as α-terpienol. After repeated recrystallization, the p-nitrobenzoate of the reduction product had mp 134-136° and failed to depress the mixed melting point (mp 134-139°) with the p-nitrobenzoate of α-terpineol, which had mp 138-139°.

Oxidation of 3-Carene with Mercuric Acetate at 23°. To a solution of 142 g of $Hg(OAc)_2$ in 4.5 liters of glacial acetic acid was added 94 g of 3-carene in drops at a temperature of 21-23°. Here the solution turned yellow and after some time a white precipitate of $(HgOAc)_2$ began to appear. The precipitate was filtered (100 g). The reaction mixture was allowed to stand at 23° overnight. The acetic acid was distilled at 28-30° (20-25 mm); the residue weighed 52.5 g. A total of 334 g of 3-carene was oxidized, employing 542 g of $Hg(OAc)_2$. We isolated 357 g (81%) of $(HgOAc)_2$ and 181 g of reaction products. The reaction products were diluted with a large amount of ether. The obtained white precipitate (44 g) was filtered and washed with ether. It is soluble in $CHCl_3$ and THF; it turns yellow when heated up to 138° and sinters at 147°, while at 158° the light yellow mass is converted to a brownish mass. Found: C 22.29; H 2.56; Hg 61.98%. $C_{18}H_{26}O_8Hg_3$. Calculated: C 22.23; H 2.67; Hg 61.93%.

Infrared spectrum (Nujol mull): 690, 860, 1020, 1050, 1260, 1320, 1470, 1590, 1630, 1725 cm^{-1}.

The addition of NaCl solution to a solution of the organomercury product in $CHCl_3$ gave a precipitate of acetoxymercury chloride, which turned black when heated up to 200°. Found: C 15.36; H 1.97; Cl 11.38; Hg 66.42. $C_{12}H_{17}O_2Cl_3Hg_3$. Calculated: C 15.98; H 1.88; Cl 11.82; Hg 66.79. Infrared spectrum (Nujol mull): 730, 850, 900, 1025, 1050, 1140, 1260, 1725 cm^{-1}.

The ether solution after removal of the organomercury compound was evaporated and the residue (134.9 g) was chromatographed in portions (5) on Al_2O_3 (neutral, IV activity). Elution with petroleum ether gave 58 g of product (n_D^{20} of the fractions 1.4860–1.4905), which consisted of acetates (II) and (III). Elution with benzene gave 24 g of product [fractions with n_D^{20} 1.5062–1.5340–1.5240; IR spectrum of one of the fractions: 820, 1025, 1050, 1140, 1185, 1255, 1380, 1450, 1520, 1610, 1660, 1690, 1735, 3020 cm^{-1}], which consisted mainly of the organomercury compound. The amount of reaction products remaining on the adsorbent was 52.9 g.

Oxidation of 3-Carene with Mercurous Acetate. To a suspension of 100 g of $(HgOAc)_2$ in 220 ml of glacial acetic acid, heated up to 90°, was added 57 g of 3-carene in drops. The reaction mixture was kept at this temperature for 5 h, the metallic mercury was separated (71 g, 91%), and the acetic acid was removed by distillation. The residue was fractionally distilled through a column with an efficiency of 17 theoretical plates. GLC analysis of the separate fractions disclosed that, besides p-methylisopropenylbenzene, they contain the acetates of p-mentha-1,5-dien-8-ol and p-mentha-1(7),5-dien-8-ol (18 g) in a ratio of 11 : 1.

Oxidation of 4-Carene with Mercuric Acetate at 22°. To a solution of 67 g of $Hg(OAc)_2$ in 840 ml of glacial acetic acid was added 30 g of 4-carene in drops. The temperature rose to 25°, and it was observed that the solution turned yellow and a white crystalline precipitate of $(HgOAc)_2$ deposited. The reaction mixture was stirred for about 2 h and then allowed to stand overnight. After filtering the $(HgOAc)_2$ and removal of the acetic acid under reduced pressure (28 mm) the reaction mixture was diluted with a large amount of ether. The precipitated organomercury compound (8 g) was filtered and purified by reprecipitation from chloroform solution with ether. The product darkens when heated up to 141°, and decomposes at 156°. Found: C 20.22; H 2.60; Hg 62.77%. $C_{18}H_{26}O_8Hg_3$. Calculated: C 22.23; H 2.67; Hg 61.93%. Infrared spectrum (Nujol mull): 835, 930, 960, 1020, 1050, 1250, 1600 very strong, 1630, 1725 cm^{-1}.

The ether solution after removal of the organomercury compound was evaporated and the residual oil (28.2 g) was chromatographed on SiO_2 (200 g). The product (4.92 g, 19 fractions) that was eluted with petroleum ether contained the acetates of p-mentha-1,5-dien-8-ol and p-mentha-1(7),5-dien-8-ol. From the product of the fraction with n_D^{20} 1.4845 (0.4 g) was obtained the adduct with maleic anhydride (0.2 g), with mp 145-147°. Its mixed melting point with the corresponding adduct of the acetate of p-mentha-1,5-dien-8-ol [1] was not depressed. The products of the saponification of the fractions with n_D^{20} 1.4860–1.4900 (3.7 g) with alcoholic caustic solution gave a mixture of the 3,5-dinitrobenzoates, from which by fractional recrystallization was isolated the 3,5-dinitrobenzoate with mp 126-128°, which failed to depress the mixed melting point (mp 126.5-128.5°) with the 3,5-dinitrobenzoate of p-mentha-1(7),5-dien-8-ol, obtained in [1].

CONCLUSIONS

1. A study was made of the oxidation of 3-carene with $Hg(OAc)_2$ in acetic acid at 23 and 86°, and with $(HgOAc)_2$ at 90°. The action of both of the oxidizing agents leads to the same acetylative oxidation products: the acetates of p-mentha-1,5-dien-8-ol and p-mentha-1(7),5-dien-8-ol.

2. The products of the oxidation of 4-carene with $Hg(OAc)_2$ in acetic acid at 20° contain the acetates of p-mentha-1,5-dien-8-ol and p-mentha-1(7),5-dien-8-ol.

3. The formation of organomercury compounds of composition $C_{18}H_{26}O_8Hg_3$ occurs when the 3- and 4-carenes are oxidized with $Hg(OAc)_2$ at room temperature.

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