OXIDATION OF 3-CARENE WITH $Pb(OAc)_4$ IN BENZENE

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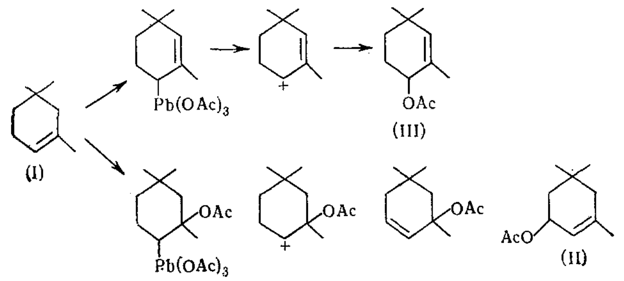
An examination of the literature data on the oxidation of olefins with lead tetraacetate discloses that the course of the reaction is explained well from the standpoint of the formation of the adduct of the lead salt with the olefin in some cases, and of the allylic organolead compound in other cases, as the intermediate compound. Especially clear in this sense is the behavior of α-cyclogeraniolene (I) [1], which when oxidized in benzene gives 3,5,5-trimethyl-Δ^2-cyclohexenyl acetate (II), while in AcOH it gives 2,4,4-trimethyl-Δ^2-cyclohexenyl acetate (III)



Scheme 1

All of this testifies to the fact that the course of the oxidation reaction with lead tetraacetate is affected not only by the structure of the olefin [2], but also by the reaction medium and the temperature.

Previously we had studied the oxidation of 3-carene under sundry conditions. A comparison of the reaction products that were isolated here with those that could be expected on the basis of the above-said regarding the influence of the medium on the reaction course makes it possible to assume that the intermediate compound when the reaction is run in benzene [3] is mainly the allylic organolead compound (VII), but together with it is formed the adduct at the double bond (XVII); in AcOH the oxidation evidently proceeds to a larger degree via the adduct, but the allylic organolead compound is also formed [4].

In Scheme 2 are shown both of the possible directions of the reaction of 3-carene (IV) with $Pb(OAc)_4$. Previously from the oxidation products of (IV) in benzene we failed to identify the alcohol acetates (XIV), (XVI) and (XXI) that could be expected according to Scheme 2. However, we could not truthfully say that these compounds are not formed, since the main purpose of the original study was the synthesis of p-mentha-1,5-dien-8-ol acetate (XI), which proved to be the main reaction product. We made a second, more careful study of the products of the oxidation of 3-carene with lead tetraacetate in benzene using the method suggested in [5] for working up the reaction mixture.

Based on the data of the IR spectra, the complex mixture of products that was obtained as an oxidation result contained, besides acetates, also ketones ($\nu_{C=O}$ 1725, 1695, 1668, 1650 cm^{-1}). We were able to identify the following carbonyl compounds: 3-acetyl-6,6-dimethylbicyclo[3.1.0]hexane (XXIII), 3,6,6-trimethyl-2,4-cycloheptadien-1-one (XXV), 4-caren-3-one (XXVI) and 4(7)-caren-5-one (XXVII). It is obvious that during the reaction course there occurred, together with acetylative oxidation, also autoxidation

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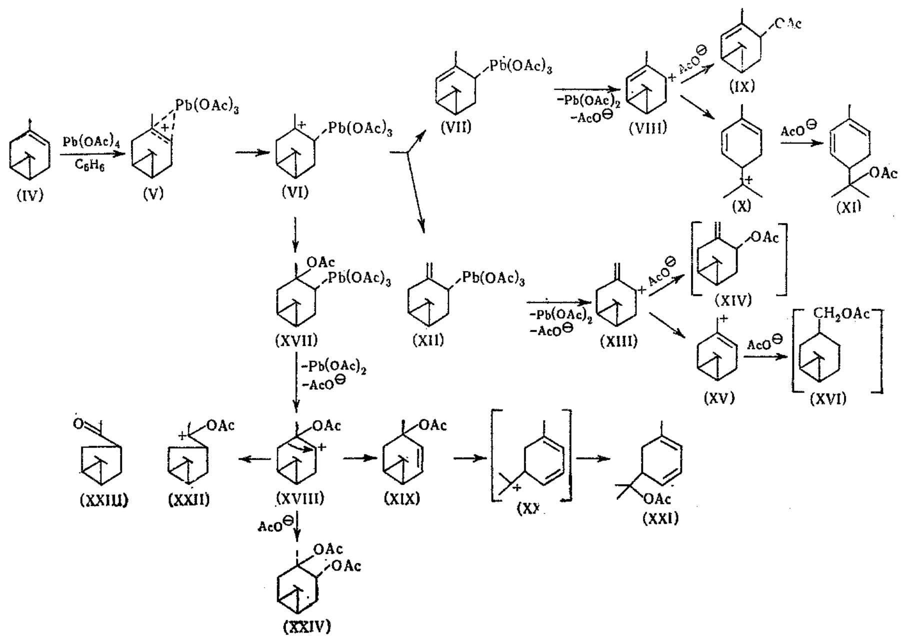
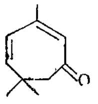
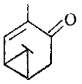
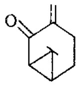


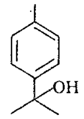
Scheme 2

of the 3-carene by atmospheric oxygen, catalyzed by lead salts, which led to the formation of carbonyl compounds [6]. As was already shown previously [3], p-mentha-1,5-dien-8-ol acetate (XI) was found as the main component. Besides it, the acetates of m-mentha-1,3-dien-8-ol (XXI) and 2-(m-tolyl)-2-propanol (XXVIII) were identified

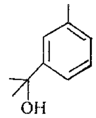

(XXV)


(XXVI)


(XXVII)



(XXVIII)



(XXIX)

The IR spectra of the saponification products of the acetate fractions testified to the presence of a secondary alcohol. We were unable to isolate this alcohol by preparative TLC and characterize it as the crystalline ester. But from the oxidation products of the mixed alcohols, using the procedure given in [7], we obtained the 2,4-dinitrophenylhydrazone (DNPH) of 4-caren-3-one [8]. Consequently, the reaction products should contain the trans-4-caren-3-ol acetate (IX) corresponding to this ketone. Since the mixture of alcohols being oxidized also contained the tertiary alcohols, p-mentha-1,5-dien-8-ol and m-mentha-1,3-dien-8-ol, which are inclined to undergo dehydration during oxidation, then the oxidation products contained, besides ketone (XXVI), also a mixture of the aromatic alcohols: 2-(p-tolyl)-2-propanol (XXVIII) and 2-(m-tolyl)-2-propanol (XXIX).

As a result, in addition to the previously identified acetates of unsaturated alcohols, the acetates of m-mentha-1,3-dien-8-ol and 2-(m-tolyl)-2-propanol were found in the products of the oxidation of 3-carene with $Pb(OAc)_4$ in benzene. Their precursor is probably 2-caren-3-ol acetate (XIX), the formation of which can be depicted only if it is assumed that adduct (XVII) is formed as an intermediate compound in the reaction. Acetates (XIV) and (XVI) were not found in the reaction products; apparently the corresponding allylic organolead derivative (XII), with an exocyclic double bond, is not formed during the course of reaction.

EXPERIMENTAL

The spectra were taken on a UR-10 instrument, while the GLC analysis was run on a Khrom-2 chromatograph, using nitrogen as the carrier gas, refractory brick as the solid support, 10% of poly-(ethylene glycol adipate) as the liquid phase, and a temperature of 138-143°.

Oxidation of 3-Carene with $Pb(OAc)_4$ in Benzene. The reaction mixture, containing 0.53 M of 3-carene and 0.306 M of $Pb(OAc)_4$ in 1 liter of benzene, was stirred at 38°. The oxidation went very slowly, and the oxidizing agent was not consumed in 31 h. The temperature was raised to 50° and 50 g of 3-carene was added; the oxidizing agent reacted completely in 22 h. The benzene solution was poured into water, and the AcOH was removed by washing in succession with water, $NaHCO_3$ solution and water, followed by drying over Na_2SO_4. The solvent was distilled off. We obtained 304 g of a mixture of products, which consisted of 244 g of volatile products and 60 g of nonvolatile products. The hydrocarbon portion was separated by distilling the reaction products from an Arbuzov flask, while the oxidation products (37.9 g) were fractionally distilled through a column with an efficiency of 17 theoretical plates (Table 1).

3-Acetyl-6,6-dimethylbicyclo[3.1.0]hexane (XXIII) and 4-Caren-3-one (XXVI). From 0.1 g of fraction 4 (see Table 1) we obtained a 2,4-DNPH mixture with mp 70-96°, which by chromatographing on Al_2O_3 (35 cm^3 of neutral product, IV activity) was separated into three 2,4-DNPH: 1) the 2,4-DNPH of 3-acetyl-6,6-dimethylbicyclo[3.1.0]hexane, mp 135-137°, the mixed melting point of which with the 2,4-DNPH of (XXIII), obtained as described in [9], was not depressed; 2) the 2,4-DNPH of 4-caren-3-one, mp 165-167.5°, which failed to depress the mixed melting point with the previously obtained [8] sample; 3) a 2,4-DNPH with mp 144-146.5°, which was not identical with the known 2,4-DNPH derivatives of the carenones.

4(7)-Caren-5-one (XXVII) and p-Mentha-1,5-dien-8-ol Acetate (XI). When 2.5 g of fractions 6-8 was chromatographed on 70 g of Al_2O_3 (neutral, IV activity) we isolated: 1) 0.3 g of substance with n_D^{20} 1.5035, which formed a 2,4-DNPH with mp 134-137.5°. The mixed melting point with the 2,4-DNPH of 4(7)-caren-5-one [10] was not depressed; 2) 0.15 g of a product with n_D^{20} 1.4972 ($\nu_{C=O}$ 1670, 1690; ν_{C-H} 2730 cm^{-1}), which formed a semicarbazone with mp 214-216°; 3) 1.2 g of a product with n_D^{20} ν1.4775 and α_D −32.8° (IR spectrum 1737, 1260 cm^{-1}), the saponification of which with alcoholic NaOH solution (0.3 g of NaOH in 60 ml of C_2H_5OH) gave an alcohol (n_D^{20} 1.4985), the 3,5-DNB of which (mp 92-93°) failed to depress the mixed melting point with the 3,5-DNB of p-mentha-1,5-dien-8-ol.

m-Mentha-1,3-dien-8-ol and 2-m-Tolyl-2-propanol. Fractions 9-16 (Table 1) (9.3 g) were chromatographed on Al_2O_3 (neutral, IV activity, 90 g); the product, eluted with petroleum ether (2.98 g, α_D −8°, IR spectrum: 710, 790, 820, 930, 980, 1027, 1145, 1250, 1520, 1615, 1672, 1740 cm^{-1}), was saponified with 3% alcoholic NaOH solution to give 2.15 g of (A), bp 65-70° (3 mm); n_D^{21} 1.4975, α_D +14°, IR spectrum: 710, 730, 795, 830, 910, 980, 1000, 1040, 1140, 1170, 1520, 1610, 1660, 1715, 3400 cm^{-1}. From the saponification product we obtained the 3,5-DNB with mp 92-93°, which was identical to the analogous p-mentha-1,5-dien-8-ol derivative. The noncrystallizing oil that was separated from this 3,5-DNB underwent partial saponification when chromatographed on Al_2O_3; the mixture of alcohols (0.3 g) that was eluted with ether gave a 3,5-DNB mixture, which by chromatographing on Al_2O_3 was separated into two products: I, with mp 100-103°, which was identical with the 3,5-DNB of m-mentha-1,3-dien-8-ol [11] (the mixed melting point was 101-104°), and II, with mp 89-92°, the mixed melting point of which with the 3,5-DNB of 2-(m-tolyl)-2-propanol [12] was not depressed.

TABLE 1

Fraction No.	Bp, °C, at 8 mm	Weight, g	n_D^{20}	α_D	Composition* (%)						
					Hydro-carbons	(XXVI)	(XXIII)	(IX, (XI), (XXI))	(XXVII)	(XXVIII), (XXIX)	XXV
1	40	2,7	1,4860	+1,3	Hydro-carbons						
2	40—43	1,85	1,4825	+1,15							
3	43—64	4,6	1,4840	−2,3							
4	88—94	0,6	1,4825	0	28,9	13,7	29,1	15,0	9,7		
5	94	0,55	1,4835	+7,6	33,9	12,8	18,3	20,0	14,6		
6	94	0,85	1,4830	+8	—	—	—	—	—	—	
7	94—95	0,45		+3,1	41,7	6,3	7,3	26,7	17,0		
8	95—96	1,25		−6	—	—	—	—	—	—	
9	96—98	1,1		−20	18,9	14,0	7,2	38,5	21,1		
10	98—100	1,1		−24	—	—	—	—	—		
11	100—101	1,15	1,4820	−27,6	32,1	15,9	7,7	32,1	11,9		
12	101	1,05	1,4822	−29,3	—	—	—	—	—		
13	101	1,4	—	−26,6	33,7	10,5	—	41,69	14,0		
14	101	1,3	—	−26,3		—	—	—	—		
15	102	0,9	—	−27,0	19,0	19,4	—	41,1	20,0		
16	102	1,3	—	−28,3		—	—	—	—	—	—
17	102,5	1,65	—	−33,3	19,6	26,8	—	27,4	—	5,2	16,8
18	103	1,5	—	−37,0	—	—	—	—	—	—	
Residue		6,7	—	—	—	—	—	—	—	—	—

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*The ratio of the components in the separate fractions was determined from the data of the GLC analysis.

Oxidation of Saponification Product A as Described in [7]. A solution of 0.4 g of the substance (n_D^{21} 1.4975, α_D +14°) in 6 ml of benzene was oxidized at room temperature with a solution prepared from 2 g of Na_2CrO_7, 1 ml of H_2SO_4 and 15 ml of H_2O. We obtained 0.3 g of product, in whose IR spectrum was present an intense band at 1675 cm^{-1} (shoulder at 1695 cm^{-1}). The oxidation products were separated by chromatographing on Al_2O_3 into 8 fractions: the first three fractions (0.1 g) contained the maximum amount of carbonyl compounds, while the subsequent fractions (0.07 g) contained alcohols. The products of the first three fractions gave a 2,4-DNPH mixture, from which by chromatographing on Al_2O_3 (neutral, IV activity) were isolated three 2,4-DNPH: 1) the 2,4-DNPH of (XXVI), mp 163-166°; 2) the 2,4-DNPH of 4(7)-caren-5-one, mp 132-136°; and 3) a 2,4-DNPH with mp 146-148°, which was not investigated in more detail.

The alcohol fractions (0.07 g) were esterified with 3,5-dinitrobenzoyl chloride; the 3,5-DNB mixture was separated by fractional crystallization into two products: 1) with mp 90.5-93°, the mixed melting point of which with the 3,5-DNB of 2-(m-tolyl)-2-propanol was not depressed; and 2) with mp 104°, which solidified at 105°, and melted again at 193-195°, and whose mixed melting point with the 3,5-DNB of 2-(p-tolyl)-2-propanol was not depressed.

CONCLUSIONS

The products of the oxidation of 3-carene with lead tetraacetate in benzene contain, besides the previously identified compounds, also the acetates of trans-4-caren-3-ol, m-mentha-1,3-dien-8-ol and 2-(m-tolyl)-2-propanol, which serves to confirm the assumption that the given reaction proceeds in two directions: a) with the formation of the allylic organolead derivative; and b) of the adduct of 3-carene with $Pb(OAc)_4$, as intermediate products.

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