ELECTROPHILIC ADDITION OF LEAD TETRAACETATE TO 2-CARENE IN AN ACIDIC MEDIUM

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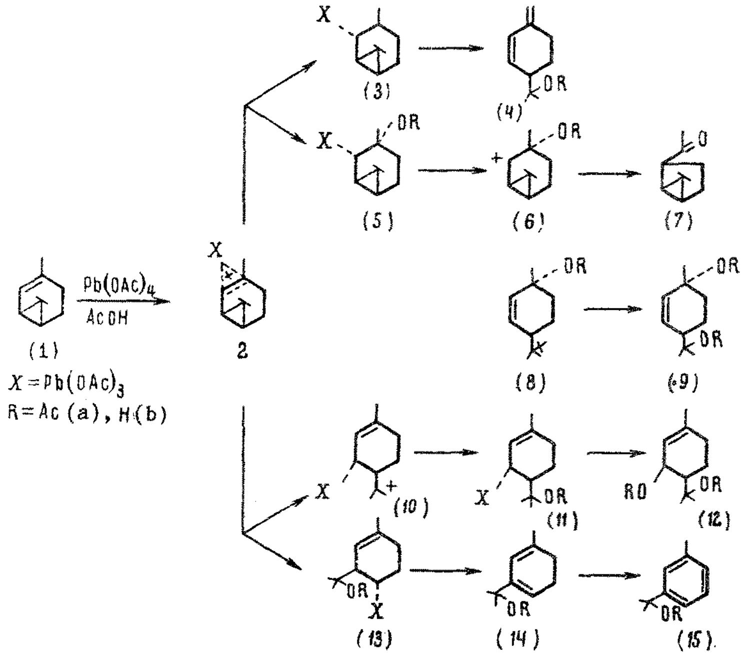
Oxidation of 2-carene by lead tetraacetate in acetic acid afforded p-menth-1(10),2-dien-7-ol, 2-acetyl-6,6-dimethylbicyclo[3.1.0]hexane, p-menth-2-ene-1α,7-diol, p-menth-1-ene-3β,7-diol, and 2-(m-tolyl)propanol-2.

Keywords: oxidation, lead tetraacetate, 2-carene, benzene, acetic acid, medium polarity.

Many researchers have noted the effect of reaction medium polarity on the course of the reaction in the oxidation of α-cyclogeraniol [1], longifolene, camphene [2], and 3-carene [3-5] by $Pb(OAc)_4$ in C_6H_6 and AcOH.

In the present work we examined the oxidation of 2-carene by $Pb(OAc)_4$ in AcOH and compared it with the results of oxidation in C_6H_6 [6]. The reaction was carried out according to [4] with the difference that the primary reaction mixture was saponified and the reaction products were identified in the form of hydroxyl-containing compounds: p-menth-1(10),2-dien-7-ol (4b), 2-acetyl-6,6-dimethylbicyclo[3.1.0]hexane (7), p-menth-2-ene-1α,7-diol (9b), p-menth-1-ene-3β,7-diol (12b), and 2-(m-tolyl)propanol-2 (15b). The pathways for the formation of these compounds are shown in the scheme below.



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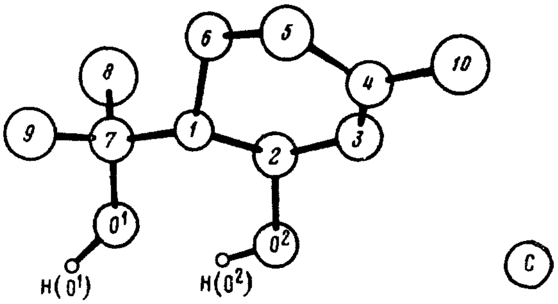

Fig. 1. Structure of p-menth-1-ene-3β,7-diol (12b).

TABLE 1. Nonhydrogen-Atom Coordinates of Molecule 12b

Atom	X	Y	Z
O^1	0.4812(4)	0.4816(3)	0.6842(3)
O^2	0.4638(4)	0.2225(3)	0.7096(2)
C^1	0.3682(4)	0.0778(4)	0.4291(4)
C^2	0.3664(5)	0.0986(4)	0.5473(3)
C^3	0.3692(4)	0.2348(4)	0.6057(3)
C^4	0.4179(4)	0.3425(3)	0.5171(3)
C^5	0.3339(4)	0.3246(4)	0.4004(3)
C^6	0.3676(5)	0.1915(5)	0.3424(3)
C^7	0.4096(5)	0.4856(4)	0.5694(3)
C^8	0.2600(6)	0.5347(5)	0.5901(5)
C^9	0.4892(6)	0.5825(4)	0.4876(5)
C^{10}	0.3665(5)	0.0615(5)	0.3739(4)

Compound 4a was isolated as the acetolysis product of allyl organolead compound 3, accompanied by homoallyl rearrangement [6]. Adduct 5 was converted via two pathways: to form ketone 7 and acetate diol 9a; the α position of the hydroxyl at C^1 indicates a cis opening of plumbonium ion 2 [7].

Since $Pb(OAc)_4$, along with the double bond, can also attack the three-membered ring [8], the formation of compounds 12a and 15a may result from rupture of bond C^1–C^7 of ion 2 in the first case and of bond C^6–C^7 in the second. Under these reaction conditions, dienol acetate 14a probably is dehydrogenated to compound 15a.

Thus, for the oxidation of 2-carene by $Pb(OAc)_4$ in C_6H_6 [6] and AcOH, the final products were dienol acetate 4a, ketone 7, and diol acetate 9a.

The reaction products did not include acetates of p-menth-1,5-dien-7-ol and p-menth-1,7-dien-3α-ol, which are formed during oxidation of 2-carene in benzene [6]. Consequently, in contrast to the oxidation of 2-carene by $Pb(OAc)_4$ in C_6H_6, oxidation in AcOH takes place along the double bond and the cyclopropane ring.

The structure of p-menth-1-ene-3β,7-diol (12b) was investigated by x-ray diffraction analysis (Fig. 1). The six-membered ring 12b is in the half-chair conformation, which is typical for most cyclohexene derivatives. Atoms C^4 and C^5 are out of the plane of the other four ring atoms by +0.46 and −0.34 Å, respectively. The hydroxyisopropyl group occupies an equatorial position. Hydroxyl group O^2H^2 is in the pseudoequatorial position and participates in the formation of intramolecular hydrogen bond O^2–H^2...O^1, which has the following parameters: O^2–H^2 0.899(2), H^2...O^1 1.82, O^2...O^1 2.61 Å, $<O^2$–H^2...O^1 145°. Because of the intermolecular hydrogen bond O^1–H^1...$O^{2'}$ [1 – X, Y + 1/2, 3/2 –Z], O^1–H^1 1.119(3), H^1...O^2 1.74, O^1...$O^{2'}$ 2.73 Å, $<O^1$–H^1...$O^{2'}$ 145°, the molecules of compound 7b in the crystal form infinite chains along the Y axis.

EXPERIMENTAL

X-ray Diffraction Analysis. Rhombic crystals; at 20°C a = 9.493(2), b = 9.994(1), c = 11.015(3) Å, d_{calc} = 1.082 g/cm³, Z = 4, $C_{10}H_{18}O_2$, pr. gr. $P2_12_12_1$.

The cell parameters and 625 independent reflections with $F^2 \geq 5\sigma$ were measured on an automatic Enraf-Nonius CAD-4 K-diffractometer (λ Mo Kα, graphite monochromator, $\omega/(5/3\theta)$-scanning, $\theta \leq 30$). The structure was decoded by the direct method using a MULTAN program and was refined by anisotropic approximation. Hydrogen atoms were detected from a differential series, and their coordinates were not refined. The final divergence factor values were $R = 0.050$, $R_W = 0.071$. All computations were carried out on a PDP 11/23 computer with an SDP program. The coordinates of nonhydrogen atoms are shown in Table 1.

IR spectra were recorded on a UR 10 instrument; PMR spectra were taken on a Varian T-60 instrument. Melting points were determined in a Koffler block. Chemapol SiO_2 was used for adsorption chromatography; thin-layer chromatography was performed using Silufol plates.

Oxidation of 2-Carene (1) with Lead Tetraacetate. A 31.7-g (0.23-mole) portion of 2-carene at 22-25°C was added dropwise to a suspension of 118.7 g (0.27 mole) $Pb(OAc)_4$ in 300 ml glacial acetic acid and 20 ml Ac_2O. The reaction mixture was mixed for 5 h at about 20°C, diluted with water, and extracted with ether. The extract was washed with water, aqueous $NaHCO_3$, and water; dried with $MgSO_4$; and evaporated. The reaction products (45.1 g) were saponified by heating (5 h, 80°C) in an alcoholic base solution (22.2 g NaOH in 288.6 ml H_2O and 1300 ml C_2H_6OH). The saponification products (29 g) were chromatographed on SiO_2.

2-Acetyl-6,6-dimethylbicyclo[3.1.0]hexane (7). A 0.2-g (0.0013-mole) sample of compound 7 was isolated from 0.5 g of a fraction eluted with petroleum ether—ether (9:1). IR spectrum (ν, cm^{-1}): 820, 955, 1020, 1140, 1170, 1250, 1365, 1600, 1630, 1710, 2870, 2940, 3010. PMR spectrum (CCl_4, δ, ppm): 0.85 s (6H, 9, 10 CH_3), 1.98 (3H, CH_3CO). 2,4-Dinitrophenylhydrazone, mp 110-113.5°C (C_2H_5OH), does not induce melting point depression in a mixture with 2,4-dinitrophenylhydrazone 7 marker [6].

p-Menth-1(10),2-dien-7-ol (4b). A 0.7-g (0.002-mole) sample of compound 4b was isolated from the fraction eluted with petroleum ether—ether (3:2). IR spectrum (ν, cm^{-1}): 820, 880, 930, 960, 1075, 1170, 1600, 1640, 3035, 3085, 3040. The 3,5-dinitrobenzoate, mp 126-127°C, melted without melting point depression when mixed with a known sample [6].

p-Menth-2-ene-1α,7-diol (9b). A 3.9-g (0.023-mole) sample of compound 9b was isolated from the fraction eluted with ether; mp 114-115°C; no melting point depression was observed in a mixture with a known p-menth-2-ene-1α,7-diol sample [6]. The IR and PMR spectra were identical with those of p-menth-2-ene-1α,7-diol [6].

p-Menth-1-ene-3β,7-diol (12b). A 4.57-g (0.027-mole) sample of compound 12b was isolated from fractions eluted with petroleum ether—ether (7:3.6:4); mp 76-77°C; no melting point depression was obtained in a mixture with a known sample [9]. The IR and PMR spectra of compound 12b were identical with those of p-menth-1-ene-3β,7-diol [9].

2-(m-Tolyl)propanol-2 (15b). A 0.1-g (0.00007-mole) sample of compound 15b was isolated from the fraction eluted with petroleum ether—ether (8:2). The 2-(m-tolyl)propanol-2 3,5-dinitrobenzoate had a mp of 90-92°C and melted without depressing the melting point in a mixture with known sample [5].

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