The Oxidation of Terpene Compounds with *t*-Butyl Chromate. IX.[1] The Oxidation of (+)-*p*-Menth-1-ene

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The oxidation of *p*-menth-1-ene with *t*-butyl chromate in carbon tetrachloride has been reported by Dupont et al.[2] to afford carvotanacetone, piperitone, and possibly 2-methyl-5-isopropyl-1, 4-hydroquinone. On the other hand, Fujita et al.,[3] in a previous paper of this series, have reported that *t*-butyl chromate oxidation of *p*-menth-1-ene in benzene yielded only carvotanacetone. We have now re-examined this oxidation in order to check the point of the oxidative attack.

The oxidation was conducted in accordance with the technique presented in a previous report of ours[3]; it has been confirmed to yield (±)-carvotanacetone (a 25% yield based on the sample taken), (+)-piperitone (26%), and traces of carvacrol, thymol and (+)-phellandric acid, by a combination of fractional distillation, column chromatography, gas chromatography, and a study of the absorption spectra and the functional derivatives. Not even a trace of the hydroquinone, which has been found by Dupont et al.,[2] could be detected.

The present results indicate that *t*-butyl chromate oxidizes equally each of two active methylenes (C-3 and C-6) of *p*-menth-1-ene to a ketone group; this differs from Fujita's results[3] on the oxidation of this hydrocarbon. The presence of phellandric acid suggests that an active methyl group at C-1 was, to a small extent, oxidized to a carboxyl, possibly via an aldehydic group. It was, moreover, noteworthy that optically inactive carvotanacetone resulted from the oxidation of an active methylene adjacent to the C*-atom in the –C*(R)=CH– system, while piperitone formed by the oxidation of the methylene in the –C(R)=CH–CH$_2$– grouping partially retained its optical activity. The same phenomenon has also been observed in the *t*-butyl chromate oxidation of (+)-limonene[4] and (+)-*p*-menth-3-ene[5]; the cause of such phenomena is not yet completely clear.

Experimental

Oxidation. — (+)-*p*-Menth-1-ene (b. p. 85°C/40 mmHg, n_D^{25} 1.4531, d_4^{25} 0.8205, $[\alpha]_D^{27}$ 96.6°) was synthesized from (+)-limonene (b. p. 85°C/40 mmHg, $[\alpha]_D^{14}$ 121.9°) by catalytic partial hydrogenation according to the method of Ref. 5 cited in Ref. 3. A benzene solution of *t*-butyl chromate was prepared from 108.6 g. of chromium trioxide, 241.6 g. of *t*-butyl alcohol, and 550 ml. of benzene following the method reported.[1,3] Then, each of this oxidant solution and (+)-*p*-menth-1-ene (50.0 g.) was simultaneously dropped into a flask over a 6 hr. period at 50°C under agitation in an atmosphere of carbon dioxide. After the mixture had been stirred for 24 hr., glacial acetic acid (70 g.) and acetic anhydride (110 g.) was added to the mixture; it was then stirred further at the same temperature for 6 hr. The treatment of the mixture according to the usual method[1,3] gave 51.0 g. of a reaction mixture, which was then fractionated into three fractions and a residue (7.6 g.) by distillation. The residue seemed to be a chromium-containing polymerized substance.

The Identification of the Oxidation Products.— 1) The first fraction (9.0 g.; b. p. 71—84°C/40 mmHg) was the unchanged hydrocarbon, judging from its gas chromatogram and infrared spectrum.

2) The second fraction (25.9 g.; b. p. 88—112°C/10 mmHg) was found to consist of equal amounts of two components by a study of its chromatostrip and by gas chromatographic analyses. This fraction was chromatographed on a silica gel column with a mixture of ethyl acetate and *n*-hexane. The first elute (b. p. 75°C/4 mmHg, n_D^{25} 1.4740, d_4^{25} 0.9382, $[\alpha]_D^{25}$ 0° (*c* 9.5, ethanol); λ_{max}^{hexane} 231 and 312 mμ (ε 12200 and 57); $\nu_{max}^{liq.}$ 1668 (C=O), 1438 (–CH$_2$CO–), 903 (>C=CH–) cm^{-1}; NMR (CCl$_4$, p.p.m. from internal tetramethylsilane) 0.81$_s$ (3H), 0.96$_s$ (3H), 1.68$_s$ (3H), 6.60$_{br}$ (1H)) gave (±)-carvotanacetone 2, 4-dinitrophenylhydrazone (m.p. and mixed m.p. 192—193°C and semicarbazone (m. p. and mixed m. p. 177—178°C).

The second elute showed the following physical properties: b. p. 78°C/3 mmHg, n_D^{25} 1.4745, d_4^{25} 0.9293; $[\alpha]_D^{11}$ +11.32° (*c* 6.5, ethanol), lit.,[6] $[\alpha]_D^{20}$ +49.8°; λ_{max}^{hexane} 225 and 332 mμ (ε 15000 and 32), lit.,[7] λ_{max}^{hexane} 225 and 333 mμ (ε 17800 and 35); $\nu_{max}^{liq.}$ 1666 (C=O), 1437 (–CH$_2$CO–), 871 (>C=CH–) cm^{-1}; NMR (CCl$_4$, p. p. m. from internal tetramethylsilane) 0.78$_d$(J=6 c. p. s., 3H), 0.88$_d$ (J=6 c. p. s., 3H), 1.87$_s$ (3H), 5.68$_s$(1H); it was confirmed to be (+)-piperitone by

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1) Paper VIII of this series: T. Matsuura and T. Suga, *J. Org. Chem.*, **30**, 518 (1965).
2) G. Dupont, R. Dulou and O. Mondou, *Bull. soc. chim. France*, **1953**, 60.
3) K. Fujita and T. Matsuura, *J. Sci. Hiroshima Univ., Ser. A*, **18**, 455 (1955).
4) K. Fujita, ibid., **24**, 691 (1960).
5) K. Fujita, This Bulletin, **34**, 968 (1961).
6) J. Read and H. G. Smith, *J. Chem. Soc.*, **1923**, 2267.
7) R. G. Cooke and A. K. Macbeth, ibid., **1938**, 1408.

preparing the 2, 4-dinitrophenylhydrazone (m. p. 117—118°C; lit.,[8] 117—118°C) and the semicarbazone (m. p. 229—230°C; lit.,[9] 226—227°C).

3) The third fraction (3.5 g.; b. p. 112—152°C/10 mmHg) was diluted with petroleum ether and shaken with a 5% sodium hydroxide solution. The extraction of the alkaline solution with ether gave a phenolic substance ($\lambda_{max}^{\text{hexane}}$ 276 and 282 mμ (ε 2000 and 2000); $\nu_{max}^{\text{liq.}}$ 3361, 1425, 1229 (OH), 3019, 1621, 1590 (aromatic), 1386, 1370 (isopropyl) cm^{-1}). It was shown, by gas chromatography using a 3 m.-column of 5.6% SE-30 on siliconized Gaschrom P at 150°C, to consist of carvacrol (t_R 6.6 min.) and thymol (t_R 6.9 min.).

4) A crystalline mass (0.25 g.) deposited from the viscid oil which was obtained as a holdup in the distilling apparatus. The recrystallization of the mass from dilute ethanol gave white needles showing a m. p. of 148—149°C ($[\alpha]_D^{25}$ +90.4° (c 1.4, methanol), $\lambda_{max}^{\text{hexane}}$ 220 mμ (ε 11000), and m/e 168 (M$^+$), 125 (M-43), 123 (M-45) and 70 (base peak) in the mass spectrum). The needles were confirmed to be (+)-phellandric acid by a comparison of their infrared spectrum in a carbon disulfide solution with that of (−)-phellandric acid (m. p. 146—147°C, $[\alpha]_D^{25}$ 109.0° (c 2.5, ethanol); $\lambda_{max}^{\text{hexane}}$ 220 mμ (ε 10800)), which was prepared from (−)-perillaldehyde in our laboratory.

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8) G. Dupont, R. Dulou and P. Crabbe, *Bull. soc. chim. France,* **1955**, 621.

9) J. C. Bardham, N. C. De and B. B. Datta, *J. Chem. Soc.,* **1951**, 3195.