NOTES

The Oxidation of (+)-p-Menth-3-ene with Selenium Dioxide

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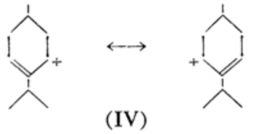
(Received March 8, 1963)

The oxidation of (+)-*p*-menth-3-ene with *t*-butyl chromate has been recorded to afford (+)-*p*-menth-3-en-2-one (major product) and (±)-*p*-menth-3-en-5-one (minor product),[1] but only the latter ketone was produced by oxidation with selenium dioxide in an alcoholic solution.[2,3] The action of selenium dioxide in acetic acid appears not to have been described as yet. We have now investigated this reaction in an 8 : 11 mixture* of glacial acetic acid and acetic anhydride in order to check the position of the oxidative attack.

The oxidation was carried out at 50°C for 40 hr. with an equimolar amount of selenium dioxide. *p*-Menth-3-en-5-yl acetate (I; 35% based on the sample taken), *p*-menth-3-en-5-ol (II; 18%) and *p*-menth-3-en-5-one (III; 8%) were obtained, all of them optically inactive. No oxidation product resulting from the attack on the other allylic methylene (2-position) could be isolated in spite of a careful examination. This finding was further supported by the fact that such successive treatments as saponification of the whole reaction products, oxidation with chromic trioxide-pyridine complex and final dehydrogenation gave thymol as the resultant. Not even a trace of carvacrol, which should be derived from C_2-oxidation products, could be detected.

The hydroxyl group of II and the acetoxy group of I apparently possessed trans-configuration with respect to the methyl group attached to C_1, as II and I were converted into the 3, 5-dinitrobenzoate which coincided with that of the (±)-*trans*-*p*-menth-3-en-5-ol characterized by Macbeth et al.[4]

In order to explain both the formation of the optically inactive oxidation products and the attack on only C_5-active methylene, we suppose the formation of a carbonium ion intermediate IV in the resonance state, when



(IV)

selenium dioxide attacks *p*-menth-3-ene. The I (major product) is explained as resulting from the reaction between IV and the solvent (i. e., the acetoxy anion). II may be formed when water, which is considered to be produced by the attack of the oxidant, reacts on IV, and then II is party oxidized to yield III.

Experimental

Sample.—(+)-*p*-Menth-3-ene[5] (b. p. 168∼169°C, n_D^{25} 1.4490, d_4^{25} 0.8080, $[\alpha]_D^{25}+114.9°$) was prepared from (−)-menthol by the pyrolysis of methyl (−)-menthylxanthate (m. p. 39.5∼40.5°C). The racemization procedure with *p*-toluenesulfonic acid[6] showed the hydrocarbon to consist of (+)-*p*-menth-3-ene (72%) and (+)-*p*-menth-2-ene (28%). However, the isolation of pure *p*-menth-3-ene was so difficult that the hydrocarbon mixture was used without further purification.

Oxidation.—To the sample hydrocarbon (41.5 g.) dissolved in a mixture of glacial acetic acid (41 g.) and acetic anhydride (56 g.), selenium dioxide (33.3 g.) was added in seven portions over a 15-hr. period at 50°C under agitation in an atmosphere of nitrogen. After the mixture had been stirred at the same temperature for a further 25 hr., it was subjected to steam-distillation. The residue seemed to be metallic selenium and a selenium-containing polymerized substance. The distillate, after being treated as usual, gave a neutral oil (26.0 g., $[\alpha]_D^{13}+3.7°$ (l, 1), E. V. 160.3), the chromato-strip chromatogram[7] of which exhibited three spots corresponding to those of I, II and III respectively.

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[1] K. Fujita, This Bulletin, **34**, 968 (1961).

[2] E. Borgwardt and E. Schwenk, *J. Am. Chem. Soc.*, **56**, 1185 (1934).

[3] R. Kitaoka, *Repts. Osaka Ind. Research Inst.* (*Ôsaka Kôgyo Gijutsu Shikenjo Hôkoku*), No. 316, 1 (1960).

* The *t*-butyl chromate oxidation of *p*-menth-3-ene[1] has been carried out in benzene containing glacial acetic acid and acetic anhydride in the same ratio as above.

[4] A. K. Macbeth, B. Milligan and J. S. Shannon, *J. Chem. Soc.*, **1953**, 2574.

[5] L. Tschugaeff, *Ber.*, **32**, 3332 (1899); W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 197 (1940).

[6] J. P. Wibaut, H. C. Beyerman and H. B. Van Leeuwen, *Rec. trav. chim.*, **71**, 1032 (1952).

[7] J. G. Kirchner, J. M. Miller and G. J. Keller, *Anal. Chem.*, **23**, 420 (1951); J. M. Miller and J. G. Kirchner, ibid., **25**, 1107 (1953).

The Identification of Reaction Products.—(1) On treating the neutral oil (8.00 g.) with an excess of 2, 4-dinitrophenylhydrazine in ethanolic hydrochloric acid, only 2, 4-dinitrophenylhydrazone (2.03 g., m. p. and mixed m. p. 145~146°C) of (±)-III was obtained.

(2) The neutral oil (5.00 g.) was treated with a 2 N hydrochloric acid solution of 2, 4-dinitrophenylhydrazine and subjected to steam-distillation in a neutral medium, and an oil (3.98 g.) containing no ketone (by the IR spectrum) was obtained. The oil was chromatographed on a silica gel column with a 17 : 3 (in vol.) mixture of isopropyl ether and *n*-hexane as the eluant, and was separated into three fractions. The first fraction (0.07 g.) was the unchanged hydrocarbon, which was found to consist of *p*-menth-3-ene and *p*-menth-2-ene by infrared spectrum comparison. The second fraction (1.92 g., b. p. 93~94°C/9 mmHg, n_D^{25} 1.4555, d_4^{25} 0.9344, $[\alpha]_D^{20}+0.12^\circ$*, $\nu_{C=O}$ 1736 cm^{-1}, ν_{C-O-} 1239 cm^{-1}) was (±)-I, which was identified by converting it into (±)-II. The third fraction (1.76 g., b. p. 92°C/10.5 mmHg, n_D^{25} 1.4770, d_4^{25} 0.9134, $[\alpha]_D^{20}$ $\pm 0^\circ$, ν_{OH} 3344 cm^{-1}, ν_{C-OH} 1028 cm^{-1}) was (±)-II, which was identified by converting it into the 3, 5-dinitrobenzoate (m. p. 141.5~142°C; lit.4), m. p. 142°C as (±)-*trans*-*p*-menth-3-en-5-yl 3, 5-dinitrobenzoate) and also into (±)-III on chromic trioxide-pyridine complex oxidation.

(3) The neutral oil (3.7 g.) was successively subjected to saponification with 0.5 N alcoholic potassium hydroxide, oxidation with chromic trioxide-pyridine complex, and dehydrogenation with palladium charcoal (palladium content: 30%) at 230°C for 15 hr. A phenolic substance (1.4 g., m. p. 49~51°C) was thus obtained, which was identified as thymol by the mixed melting point determination. The gas chromatogram of the substance did not show the peak corresponding to carvacrol, but a single peak was observed.

Summary

The oxidation of (+)-*p*-menth-3-ene by selenium dioxide in a mixture of glacial acetic acid and acetic anhydride was examined with special attention paid to the position of the oxidative attack, i. e., the C_2- or C_5-position of the hydrocarbon. Careful examination of the reaction product showed that this oxidation yielded only (±)-*p*-menth-3-en-5-yl acetate (major product), (±)-*p*-menth-3-en-5-ol and (±)-*p*-menth-3-en-5-one. Thus, this oxidant selectively attacks an active methylene group at the C_5-position of *p*-menth-3-ene.

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* Judging from the gas chromatogram, which exhibited a small peak of the sample hydrocarbon in addition to a main peak of the acetate, the ester was contaminated with a small amount of the unchanged hydrocarbon. Accordingly, this small optical rotation value is due to the hydrocarbon.