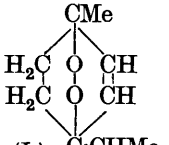
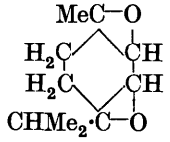
CCCLXIV.—*The Oxidation of α-Terpinene with Benzoylhydroperoxide.*

By LESLIE ALDERMAN ELSON, CHARLES STANLEY GIBSON, and JOHN LIONEL SIMONSEN.

IT was suggested by Nelson (*J. Amer. Chem. Soc.*, 1911, **33**, 1404; 1913, **35**, 84) that the isomeric substance which is formed when ascaridole (I) is heated at 150° is the dioxide (II). It appeared that it might be possible to synthesise this substance by the oxidation of α-terpinene with benzoylhydroperoxide (compare Prileschaev, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1387, and subsequent papers; Meerwein, *J. pr. Chem.*, 1926, **113**, 14). A synthesis of this dioxide would be of special interest, since it does not appear

unlikely that it might have the constitution (III), the intermediate formation of which is postulated by Nelson during the hydration to ascaridole glycol (IV).


(I.)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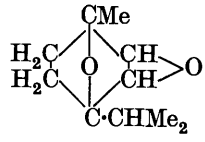
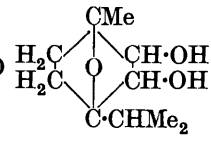
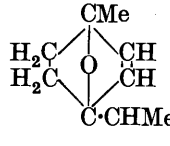
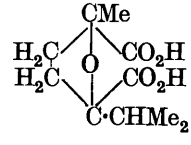

(III.)


(IV.)

Unfortunately, α-terpinene cannot be obtained free from *p*-cymene and the isomeric terpinenes. The specimen used by us had been prepared by Dr. T. A. Henry and Mr. H. Paget from a supposed Russian oil of turpentine. It had constants agreeing well with those usually found for ordinary terpinene, and the yield of nitrosite (see below) was comparatively high. When the terpene was treated with benzoylhydroperoxide the oxidation proceeded rapidly but addition of only one atom of oxygen occurred. The product contained, in addition to *p*-cymene, present to the extent of 30% in the original oil, and complex substances which could not be identified, chiefly 1 : 4-*oxido*-Δ^2-p-*menthene* (V), the constitution of which was proved by its oxidation to 1 : 4-cineolic acid (VI). Addition to α-terpinene took place, therefore, in the 1 : 4-positions and the projected synthesis could not be realised.

(V.)




(VI.)

Experimental.

The terpinene used had, after distillation over sodium, b. p. 173—180°, $d_{21}^{23°}$ 0·8529, $n_D^{23°}$ 1·4748. From 3 c.c. of the oil, 0·2 g. of the crystalline nitrosite could be prepared.

The terpene (16 g.) was added to a solution of benzoylhydroperoxide in chloroform (2 l.; 100 c.c. = 0·19 g. of available oxygen) at 0°. After 1 hour, titration showed that approximately one-half of the available oxygen had been used; no further change took place after the mixture had been kept for a further 48 hours below 8°. An additional quantity of the terpene (16 g.) was added and after 12 hours the chloroform solution, having been washed with sodium hydroxide solution (10%) until free from benzoic acid, was dried, and the chloroform removed, a long column being used. The residual oil was subjected to prolonged fractional distillation under diminished pressure, difficulty being experienced in the

earlier fractionations owing to the presence of a substance which lost water. Ultimately, three fractions were obtained: (i) b. p. 175—177°/768 mm., $d_{21}^{22\cdot}$ 0·8644, $n_D^{22\cdot}$ 1·4810; (ii) b. p. 115—117°/50 mm., $d_{21}^{21\cdot}$ 0·9281, $n_D^{21\cdot}$ 1·4728, $[R_L]_D$ 45·90; and (iii) a fraction which boiled irregularly from 135—180°/50 mm.

Fraction (i), which comprised about 30% of the total distillate, consisted of *p*-cymene, which was identified by analysis and by oxidation to *p*-α-hydroxy*iso*propylbenzoic acid.

Fraction (ii). 1 : 4-*Oxido*-Δ^2-p-*menthene*. The oxide was a somewhat thick, colourless oil having a faint camphoraceous odour (Found: C, 79·6; H, 10·6. $C_{10}H_{16}O$ requires C, 79·0; H, 10·5%). It was only very slowly attacked by potassium permanganate in acetone solution, but in the presence of alkali the oxidation proceeded readily. The oxide (14 g.) was suspended in sodium carbonate solution (Na_2CO_3, 5 g.) and, after being cooled to 0°, treated with aqueous potassium permanganate (2·5%) (mechanical stirring) until a permanent pink colour was obtained, carbon dioxide being passed through the solution during the reaction. After distillation in steam to remove a small quantity of volatile oil, the solution was filtered and evaporated to dryness in a current of carbon dioxide. The residual salts were extracted with chloroform, to remove neutral products of the reaction (A), and dissolved in a little water; after acidification, a partly crystalline acid separated. This was dissolved in ether, the ethereal extract dried and evaporated, and the crystalline residue dried on porous porcelain. The solid, m. p. 112—115°, was recrystallised from water, in which it was somewhat sparingly soluble, and was obtained in colourless needles, m. p. 121—122°. It was identified as 1 : 4-cineolic acid by analysis (Found: C, 55·8; H, 7·7. Calc.: C, 55·5; H, 7·4%) and by the method of mixed melting point. From the porous plate on which the cineolic acid had been drained, a liquid acid was extracted which did not crystallise and was not identified.

The chloroform solution (A) gave on removal of the solvent a viscid oil, which was readily soluble in all the ordinary solvents except light petroleum. It could not be obtained crystalline and the benzoyl derivative also was an oil.

Fraction (iii) was apparently a complex mixture and no fraction of constant boiling point could be separated. A fraction, b. p. 125—135°/24 mm., which should have contained any dioxide which might have been formed in the reaction, had $d_{21}^{21\cdot}$ 0·9654 and $n_D^{21\cdot}$ 1·4707. It gave on analysis figures which showed it to be a mixture (Found: C, 75·5; H, 10·0%). On distillation in steam it was apparently decomposed with formation of *p*-cymene and a much less volatile oil. The latter, b. p. 160—180°/28 mm., $n_D^{21\cdot}$ 1·528,

was a viscid yellowish oil and consisted apparently of a diterpene (Found: C, 87·9; H, 11·9. Calc.: C, 88·2; H, 11·8%). When dissolved in acetic anhydride, it gave with sulphuric acid a transient purple coloration passing into a deep red.

In the preliminary fractionation of the oil a small fraction, distilling above 180°/20 mm., was separated which on keeping deposited a few mg. of a crystalline solid. This crystallised from light petroleum in feathery leaflets, m. p. 110—112°, but the quantity was insufficient for analysis.

We wish to express our thanks to Dr. T. A. Henry for the terpinene used in these experiments and for the specimen of 1 : 4-cineolic acid used for comparison purposes. The cost of this investigation has been met by a grant from the Government Grant Committee of the Royal Society, which is also gratefully acknowledged.

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