193. *β-Phellandrene Tetrabromide.*

By P. A. Berry and A. Killen Macbeth.

The optically active tetrabromide isolated from the terpene fraction of *E. cneorifolia* oil is derived from *l*-*β*-phellandrene and is identical with samples prepared from *l*-*β*-phellandrene derived from Canada-balsam oil. *d*-*β*-Phellandrene from water-fennel oil also forms an optically active tetrabromide. The *β*-phellandrene tetrabromides are characterised by rotations of opposite sign to that of the hydrocarbon from which they are derived.

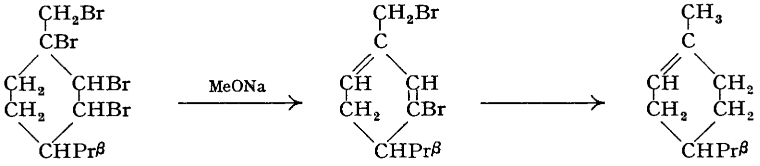
In a previous paper (Berry, Macbeth, and Swanson, *J.*, 1937, 1443) it was shown that a seasonal variation occurred in the oil of *Eucalyptus cneorifolia* with an increase in the terpene content from a minimum of some 10% to a maximum approaching 50% which is attained during the period of active growth in the early summer months. The presence of *l*-α- and *l*-β-phellandrene was established, and after further examination of the terpene fraction it was reported by Berry and Macbeth (*Nature*, 1945, **156**, 175) that a crystalline tetrabromide can be isolated after bromine vapour has been aspirated through solutions of such terpene fractions in acetic acid, and the reaction mixture stored for some days in the refrigerator. The crystalline tetrabromide is separated in amounts corresponding with upwards of 20% of the total terpene when the hydrocarbon is dissolved in about four times its weight of acetic acid, and excess of bromine introduced whilst the temperature is kept below 0°.

Analysis of the *tetrabromide* showed the formula to be $C_{10}H_{16}Br_4$, and in view of the fact that the substituent groups in the cyclic compounds occurring in *E. cneorifolia* oil are in the para-positions it may reasonably be concluded that the progenitor of the tetrabromide is a *p*-menthadiene. Of the fourteen possible structures seven inactive compounds are excluded as the tetrabromide is dextrorotatory, and of the remaining seven only two (limonene and *p*-mentha-2 : 8(9)-diene) are optically active and without conjugated double bonds. Henry and Paget (*J.*, 1925, **127**, 1649) isolated from oil of chenopodium an inactive tetrabromide which they considered was derived from *p*-mentha-2 : 8(9)-diene. We have confirmed this observation excepting that our tetrabromide had slight optical activity. The tetrabromides from limonene and dipentene have also been re-examined, and as their properties differ markedly from those of the tetrabromide from *E. cneorifolia* these substances must also be excluded. One is therefore forced to consider the para-menthadienes containing a conjugated system of double bonds despite the fact that crystalline tetrabromides derived from such substances are not described in the literature.

The tetrabromide now described is debrominated by magnesium in ether and yields a hydrocarbon, $C_{10}H_{16}$, which is readily converted into the tetrabromide again. This hydrocarbon showed the characteristics of *l*-β-phellandrene; in particular it formed a nitrosite the mutarotation of which was similar to that of the nitrosite derived from a sample of *l*-β-phellandrene from Canada-balsam oil. Authentic samples of *l*-β-phellandrene gave tetrabromides identical with that derived from the terpene fractions of *E. cneorifolia* oil, in particular having m. p. 118—119° after recrystallisation from ethyl acetate and a specific rotation of approximately +49° in the same solvent, the value being unchanged even after two months. The specific rotation in chloroform was higher (+53·6°) and these solutions too showed little change in rotation on storage.

The chief feature of the tetrabromide derived from β-phellandrene is the change of sign of rotation, the lævorotatory hydrocarbon giving a dextrorotatory tetrabromide. This characteristic property provides a convenient and useful criterion for β-phellandrene, the identification of which has hitherto mainly rested on the optical properties of derivatives such as the nitrosite. A sample of *d*-β-phellandrene from water-fennel oil was available (Berry, Macbeth, and Swanson, *J.*, 1937, 1448), and this yielded a tetrabromide having m. p. 118—119° which had a specific rotation of the same magnitude as that derived from *l*-β-phellandrene but of opposite sign.

Wallach (*Annalen*, 1894, **281**, 129) examined the debromination of limonene tetrabromide by sodium methoxide and obtained as a product a monobromo-compound which nascent hydrogen converted into carveol methyl ether. The reaction with β-phellandrene tetrabromide (I) follows quite a different course, as only two bromine atoms are removed by the methoxide, and nascent hydrogen converts the product into a lævorotatory hydrocarbon of low density having the composition $C_{10}H_{18}$. The reactions appear to result in the formation of *l*-*p*-menth-1-ene (II), as the molecular refraction (45·85) agrees with the calculated value (45·7) and the compound forms a nitrosochloride having m. p. 93—94° and $[\alpha]_D$ $-342°$ (ether). The nitrosochloride derived from *d*-*p*-menth-1-ene (Wallach, *Annalen*, 1911, **381**, 58; Vavon, *Compt. rend.*, 1911, **152**, 1675) has m. p. 95—96° and $[\alpha]_D$ $+344°$, the sign of rotation of the derivative being the same as that of the parent hydrocarbon.



(I.) (II.)

Experimental

Tetrabromide from Terpene Fraction of E. cneorifolia *Oil.*—Preliminary experiments showed that the amount of tetrabromide formed varied greatly with conditions, and the factors favourable to high yield were mainly (1) the use of freshly distilled terpene fraction dissolved in about four times its volume of acetic acid, (2) a bath temperature below 0° but not so low as to cause much crystallisation of acetic acid on the walls of the reaction vessel, (3) steady aspiration of bromine vapour at such a rate that bromination was completed within an hour and the additional excess of bromine introduced for a further fifteen minutes, (4) efficient stirring to ensure that the temperature of the reaction mixture did not rise above about 5°, and (5) subsequent storage in the refrigerator for several days.

In a typical experiment freshly distilled terpene (100 c.c.) having α_D $-42·4°$ (homogeneous) was dissolved in acetic acid (350 c.c.) and brominated for 70 minutes, the flask being immersed in an ice–salt mixture. Bromine (140 g.) was rapidly absorbed during 45 minutes and aspiration was stopped after an excess (180 g. in all) had been introduced (70 minutes). The mixture was placed in the refrigerator, and crystallisation of the tetrabromide was beginning within an hour. After five days the crystals were removed at the pump and washed with cold acetic acid. Yield, 56 g. of crude tetrabromide having m. p. 109—110°, $[\alpha]_D$ 57·1° in chloroform (*c*, 4·468). This is equivalent to upwards of 20% of the terpene taken.

In another experiment terpene (100 c.c.; α_D $-43·2°$) in acetic acid (400 c.c.) was brominated by aspiration of bromine (195 g.) for an hour, the temperature of the bath being $-8°$. Some acetic acid crystallised on the walls during reaction and the yield of crude washed tetrabromide collected after seven days was 47 g. having m. p. 109—111, $[\alpha]_D$ 59·5°. In a further experiment terpene (75 c.c., α_D $-38°$) in acetic acid (300 c.c.) after treatment in a similar way with bromine (147 g.) gave crude washed tetrabromide (37·3 g.) having m. p. 108—110°, $[\alpha]_D$ 52·7° in chloroform. This corresponds with about 18% of terpene taken.

The combined yields of tetrabromide (140 g.) from the above preparations after four crystallisations from ethyl acetate gave pure tetrabromide as flat glistening plates having m. p. 116—117°, $[\alpha]_D$ 53·6° in chloroform (*c*, 5·41). Further recrystallisation raised the m. p. to 118—119°. The solubility in ethyl acetate at 17° is 10·4% w/w and tetrabromide of good quality can be recovered as a first crop after concentration of the mother liquors. The specific rotation of the *tetrabromide* in ethyl acetate is somewhat lower than in chloroform, a solution (*c*, 4·004) having a value of 48·8° which was unchanged after the solution had been kept for two months (Found: C, 26·4; H, 3·65; Br, 70·2. $C_{10}H_{16}Br_4$ requires C, 26·3; H, 3·5; Br, 70·1%).

Debromination of the Tetrabromide.—The method of debromination used was essentially that described by Brown and Lemke (*Ber.*, 1923, **56**, 1562) in the preparation of limonene from its tetrabromide by the action of magnesium in ether. Purified tetrabromide (39 g.) in anhydrous ether (196 c.c.) was gently warmed with magnesium (6·2 g.) and a trace of iodine. After 90 minutes the ethereal layer was separated and washed with water (twice), and the washings were used to wash the original lower (magnesium bromide) layer. The separated ether from this was washed with water and the total ether distilled to remove solvent and then steam distilled. From two such experiments unchanged tetrabromide (5·3 g.) was recovered from the steam-distillation flask, and an oil (15·8 g.) of low density (*d* 0·843) was recovered from the distillate. The hydrocarbon obtained on distilling the oil over sodium had $d^{15°}_{15°}$ 0·8411 and $[\alpha]^{20°}_D$ $-16·2°$. It had the formula $C_{10}H_{16}$ and gave a nitrosite (Found: C, 88·3; H, 11·95. Calc.

C, 88·15; H, 11·8%). When brominated as described above the hydrocarbon gave a tetrabromide identical with the original.

Tetrabromide of l-*β-Phelladrene.*—The formation of a nitrosite suggested that the hydrocarbon was possibly a phellandrene, and this was supported by the fact that a terpene fraction from which the phellandrene was removed gave, on bromination, only a small quantity of crystals which were inactive and had m. p. 220°. This was evidently benzene hexabromide derived from traces of benzene in the solvents used during removal of the phellandrene as nitrosite. The bromination of *l*-*β*-phellandrene was therefore examined, the material being available as an old sample derived from Canada-balsam oil. On steam distillation this gave terpene having α_D $-42°$, and after bromination as described above crude tetrabromide (7·2 g.) was obtained in amount equivalent to about 10% of the terpene. It had m. p. 110—112°, $[\alpha]_D^{20°}$ 57·3° in ethyl acetate (*c*, 4·265), and after several recrystallisations from the same solvent the m. p. had risen to 116—117°. The sample showed no depression of m. p. on admixture with the pure tetrabromide derived from *E. cneorifolia* oil.

A small sample of the residue from water fennel oil from which *d*-cryptone and *d*-phellandral had been removed some years before was steam distilled, and the terpene collected (which contained *d*-*β*-phellandrene and was dextrorotatory) was brominated in the usual way. The crude tetrabromide of *d*-*β*-phellandrene had m. p. 111—113° and a high lævo-rotation ($[\alpha]_D$ $-56·6°$) in ethyl acetate (*c*, 5·492). After four recrystallisations from ethyl acetate the pure tetrabromide had m. p. 116—116·5°, and $[\alpha]_D^{20°}$ $-55·1°$ in ethyl acetate (*c*. 4·046). The m. p. of the substance is the same as that of the tetrabromide of *l*-*β*-phellandrene and its optical activity of the same order, but of opposite sign.

The tetrabromide of *dl*-*β*-phellandrene was separated as long needles when a solution of equimolecular amounts of the *d*- and the *l*-compound in ethyl acetate was allowed to evaporate slowly. The substance was inactive and had m. p. 112—113°, not changed by further crystallisation.

Debromination by Sodium Methoxide.—The tetrabromide of *l*-*β*-phellandrene (50 g.) was refluxed for more than 8 hours with sodium methoxide (8 g. sodium in 100 c.c. of methyl alcohol). After the addition of some water the reaction mixture was steam distilled, and the oil (30 g.) recovered from the distillate was dried (KOH) and fractionated under reduced pressure. It distilled as a main fraction (28 g.) which was again refluxed for 7 hours with sodium methoxide, and the oil was worked up again giving a main fraction (26 g.) which distilled at 144—148°/11 mm. and had *d* 1·448; $[\alpha]_D$ 19·2°; $n_D^{15°}$ 1·5643. Bromine combined as sodium bromide in the still residue after the steam distillations amounted in the first case to 18·5 g. which is equivalent to the removal of 2·1 atoms of bromine from the tetrabromide. After the second treatment with methoxide bromine removed was assayed as equivalent to a further 0·2 atom only.

The partly debrominated oil (24 g.) was dissolved in absolute alcohol (250 c.c.) and gradually treated with sodium (20 g.), the mixture being heated on the water-bath as reaction slowed down. The oil collected on steam distillation still contained bromine and was again subjected to the action of nascent hydrogen. The oil then collected on steam distillation, after being dried (KOH), distilled at 75—76°/34 mm. and had $d_{15.5°}^{21°}$ 0·8228; $[\alpha]_D$ $-81·2°$ (homogeneous); $n_D^{21°}$ 1·4581 (Found: C, 87·2; H, 13·0. Calc. for $C_{10}H_{18}$: C, 86·85; H, 13·1%). The oil readily decolorised bromine in acetic acid and gave a nitrosochloride, m. p. 93—94°, which was very stable and did not decompose on heating to 140°. In ether (*c*, 0·714) the nitrosochloride had $[\alpha]_D$ $-342°$ which had fallen after 13 hours to $-322°$ and after 85 hours to $-280°$. It appears that the compound is *l*-*p*-menth-1-ene as the constants are in good agreement with those recorded for *d*-*p*-menth-1-ene, the optical values being of opposite sign.

Other Tetrabromides.—In the course of the work several tetrabromides were prepared for comparison with the product obtained from *E. cneorifolia* oil. *d*-Limonene tetrabromide was prepared from sweet orange oil of pharmaceutical quality, and had m. p. 104—105°, $[\alpha]_D$ 79·2° in chloroform. Dipentene tetrabromide was prepared from a sample of dipentene kindly supplied by Professor T. G. Jones, and a further preparation was carried out from cineol. The tetrabromide was inactive and had m. p. 126—127°. A tetrabromide was also prepared from an imported sample of pharmaceutical oil of chenopodium; it had m. p. 115—116°, $[\alpha]_D$ 2·2° in chloroform (*c*, 16·13) (compare Henry and Paget, *loc. cit.*).

JOHNSON CHEMICAL LABORATORIES, UNIVERSITY OF ADELAIDE. [*Received, October 23rd,* 1946.]