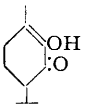
184. p-*Menthane-2 : 3-diols. Part I. The Hydroxylation of* (±)-cis- *and* (±)-trans-*Menth-2-enes.*

By A. Killen Macbeth and W. G. P. Robertson.

(±)-*trans*- and (±)-*cis*-Menth-2-enes have been prepared and hydroxylated with osmium tetroxide and with peracetic acid. The use of osmium tetroxide apparently results in the formation of a single epimer in each case. Peracetic acid produces a mixture of the two possible *trans*-glycols from (±)-*trans*-menth-2-ene but one epimer predominates. The isolation of three glycols from the peracetic acid hydroxylation of (±)-*cis*-menth-2-ene appears to be due to the presence of traces of (±)-menth-3-ene.

Very little has been recorded about the *p*-menthane-2 : 3-diols: no attention has been devoted to their stereochemistry. The diols themselves become available by either of two principal methods, for diosphenol (I) may be reduced under different conditions, and the menth-2-enes may be hydroxylated by a variety of oxidising agents.

Kondakov and Bachtshiev (*J. pr. Chem.*, 1901, **63**, 49), by reduction of diosphenol with sodium and ethanol, obtained $(\pm)$-menthol and two glycols, one of which was crystalline (m. p. 92°). Semmler and McKenzie (*Ber.*, 1906, **39**, 1160) by the same reaction also isolated the glycol mixture but were unable to confirm the production of $(\pm)$-menthol: and since permanganate oxidation of the glycol gave α-methyl-α′-*iso*propyladipic acid (III) its structure as a *p*-menthane-2 : 3-diol (II) was established.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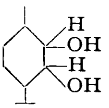
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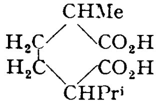

(III)

Cusmano and Boccucci (*Gazzetta*, 1923, **53**, 649) also claimed to have isolated a mixture of two keto-alcohols together with crystals of what was probably a glycol when the product resulting from the hydrogenation of diosphenol in ether at ordinary temperatures in the presence of platinum black was fractionated. Walker and Read (*J.*, 1934, 238) also studied the hydrogenation of diosphenol but did not report the formation of a glycol.

The hydroxylation of $(+)$-*trans*-*p*-menth-2-ene has been studied by Hückel and his co-workers. Hückel and Kummerle (*J. pr. Chem.*, 1942, **160**, 74) obtained a glycol fraction when the menthene was oxidised with lead tetra-acetate, and isolated a bisphenylurethane, m. p. 149—151°. They also prepared a bisphenylurethane, m. p. 83—85°, from a glycol mixture which had previously been obtained on oxidation of the menthene by perbenzoic acid followed by treatment of the oxide with perchloric acid (Hückel, Tappe, and Legutke, *Annalen*, 1940, **537**, 222). In no case were any of the glycols further examined.

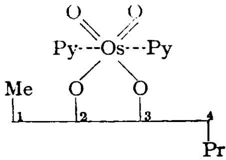
By reduction with sodium and ethanol of a 2-hydroxymenthone, obtained by hydrolysis of the 2-acetoxymenthone prepared by the acetoxylation of $(-)$-menthone with mercuric acetate, Treibs and Bast (*Annalen*, 1949, **561**, 165) obtained a glycol, m. p. 92°, which was optically active. The identity of this glycol with that obtained by Kondakov and Bachtschiev (*loc. cit.*) from diosphenol by reduction with sodium and ethanol as suggested by Treibs and Bast (*loc. cit.*) is open to doubt as diosphenol is optically inactive.

The stereochemistry of the *p*-menthane-2 : 3-diols is not too simple a question as owing to the presence of the four asymmetric carbon atoms eight epimers are possible, and these may occur in inactive or optically active forms. As the stereoisomerism of the menthols has been established (Zeitschel and Schmidt, *Ber.*, 1926, **59**, 2303; Read, Robertson, and Cook, *J.*, 1927, 1276; Read and Grubb, *J.*, 1934, 313, 1779; McNiven and Read, *J.*, 1952, 153) the configurations of the diols will be designated on the basis of that of the menthols, and the spatial arrangement of the 2-hydroxyl group relative to the 3-hydroxyl group of the parent menthol will be specified as *cis* or *trans*. On this system the *p*-menthane-2 : 3-diols are referred to as 2-hydroxymenthols.

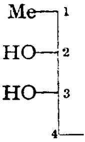
In considering the possibility of synthesising and characterising the 2-hydroxymenthols several stereochemically specific methods appear to be available. The hydroxylation of a suitable *cyclo*hexene by peracids, for example, is likely to result mainly in the formation of the *trans*-glycol (English and Gregory, *J. Amer. Chem. Soc.*, 1947, **69**, 2120), the hydrolysis of the intermediate *cis*-epoxide involving a Walden inversion (Swern, *Chem. Reviews*, 1949, **45**, 51). On the other hand, hydroxylation by the action of osmium tetroxide has been shown to yield the *cis*-glycol alone (Criegee *et al.*, *Annalen*, 1936, **522**, 75; 1942, **550**, 99).

The $(\pm)$-*cis*- and *trans*-menth-2-enes do not appear to have been described previously. $(\pm)$-*cis*-Menth-2-ene was prepared from $(\pm)$-*iso*menthol through the toluene-*p*-sulphonate, which was converted into the menthene on treatment with sodium ethoxide (cf. Hückel and Wagner, *Ber.*, 1941, **74**, 662); $(\pm)$-*iso*menthol was obtained by the catalytic hydrogenation of thymol in the presence of a nickel catalyst (Hückel and Niggemeyer, *Ber.*, 1939, **72**, 1357). $(\pm)$-*trans*-Menth-2-ene was similarly derived from $(\pm)$-menthol.

Oxidation of $(\pm)$-*trans*-menth-2-ene with osmium tetroxide (Cook and Schoental, *J.*, 1948, 170) gave an oil, but the work was necessarily carried out on too small a scale to permit rigid purification of the glycol. The oil readily yielded a di-*p*-nitrobenzoate, and the ease with which the ester was purified suggests that oxidation with osmium tetroxide yields only one of the two possible *cis*-glycols. Since the oxidation takes place through the formation of a complex (IV) and since steric hindrance of the *iso*propyl group at $C_{(4)}$ may be presumed to prevent appreciable formation of the *neo*menthol-diol, there appear to be reasonable grounds for assuming that the product is (±)-*cis*-2-hydroxymenthol (V). Oxidation of (±)-*cis*-menth-2-ene with osmium tetroxide also gave an oil, which similar considerations suggest is (±)-*cis*-2-hydroxy*iso*menthol (VI). The oil readily gave a crystalline di-*p*-nitrobenzoate.



(IV; Py = Pyridine)



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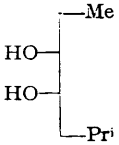

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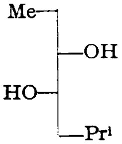

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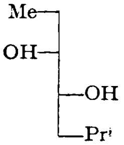

(VIII)

Attempts to hydroxylate the menthenes to diols with sodium chlorate in the presence of catalytic amounts of osmium tetroxide (Milas and Terry, *J. Amer. Chem. Soc.*, 1925, **47**, 1412; 1926, **48**, 2647) failed. It is probable that oxidation proceeded beyond the glycol stage. Milas and Sussman (*J. Amer. Chem. Soc.*, 1937, **59**, 2345) obtained *cis*-*cyclo*hexane-1 : 2-diol in 58% yield from *cyclo*hexene by hydroxylation with hydrogen peroxide in *tert.*-butanol with osmium tetroxide as catalyst: no pure glycol could be obtained from (±)-*trans*-menth-2-ene by this method, fractional distillation of the product yielding an oil which could not be crystallised but, judged by its high viscosity, may have contained some glycol; attempts to prepare a di-*p*-nitrobenzoate were, however, unsuccessful. The modified procedure of Cook and Schoental (*J.*, 1950, 47) for hydroxylation with hydrogen peroxide with osmium tetroxide as catalyst was also unsuccessful with the menth-2-enes. Attempts to hydroxylate the menth-2-enes with potassium permanganate at *ca.* −40° also failed.

Peracetic acid was selected for the hydroxylation of the menthenes instead of the perbenzoic acid used by Hückel, Tappe, and Legutke (*loc. cit.*). With this reagent (±)-*trans*-menth-2-ene yielded a mixture of glycols as a very viscid colourless oil after hydrolysis of the intermediate monoacetates. The purified glycol obtained on fractionation could not at first be induced to crystallise, and so was converted into the di-*p*-nitrobenzoate. On hydrolysis of the ester, and extraction of the glycol with light petroleum (b. p. 40—60°) a crystalline glycol (A) separated, having m. p. 79°. In view of the evidence in favour of *trans*-hydroxylation by peracids (see above) this is either *trans*-2-hydroxymenthol (VII) or *trans*-2-hydroxy*neo*menthol (VIII), but at present it is not possible to distinguish between them. The pure glycol, m. p. 79°, gives a di-*p*-nitrobenzoate, m. p. 168°. A small amount of a second di-*p*-nitrobenzoate (m. p. 118°) was subsequently isolated, but the amount was insufficient to permit isolation of the pure glycol (B) on hydrolysis.

As the configuration of the glycols obtained by the hydroxylation of (±)-*trans*- and (±)-*cis*-menth-2-ene cannot be specified completely they will, for the present discussion, be referred to as glycol A, B, etc., as listed in the Table.

Hydroxylation of (±)-*cis*-menth-2-ene with peracetic acid yielded a glycol mixture as a very viscid oil which when fractionally distilled under reduced pressure gave two fractions which partly crystallised. Esterification of portions of each of these fractions with *p*-nitrobenzoyl chloride gave a mixture of two esters separable by fractional crystallisation into di-*p*-nitrobenzoates, m. p. 166° and 152—153°. Fractional crystallisation of the two diol fractions from light petroleum yielded a glycol C, m. p. 78—78·5°, which gave a di-*p*-nitrobenzoate, m. p. 137°, and a glycol D, m. p. 69°, which gave a di-*p*-nitrobenzoate, m. p. 152—153°, identical with the similar ester obtained from the crude distilled glycol mixture. The residual glycol recovered from the light petroleum mother-liquors was a viscid colourless oil which partly crystallised after several weeks; draining, followed by recrystallisation, then gave a glycol E, m. p. 77°, whose di-*p*-nitrobenzoate, m. p. 166°, was identical with the similar ester previously obtained from the fractionated glycol.

The possibility that one of the three diols obtained above from (±)-*cis*-menth-2-ene is a eutectic seems remote, as all the esters isolated were very readily purified; and it seems more probable that the third glycol is derived from a menth-3-ene, present as an impurity in the menth-2-ene used. On this view glycol C is most likely to be derived from the menth-3-ene, as in the hydroxylation the diols C, D, and E were isolated in the ratio 2 : 6 : 5. It appears that it is also difficult to obtain a pure sample of menth-3-ene as Hückel, Tappe, and Legutke (*loc. cit.*) have shown that what was previously regarded as pure (±)-menth-3-ene (Tschugaev, *Ber.*, 1899, **32**, 3332; Malcolm and Read, *J.*, 1939, 1037) contains some 30% of (±)-menth-2-ene. It is therefore not surprising that a sample of hydrocarbon, obtained by nitrous acid deamination of (±)-*iso*menthylamine and consisting largely of (±)-menth-3-ene, also led after hydroxylation with peracetic acid to the di-*p*-nitrobenzoates of the three glycols C, D, and E : but the relative amount of the C-ester was in this case very much higher. The scanty knowledge of the menthane-3 : 4-diols is of no help in assigning such a structure to glycol C. Hock and Lang (*Ber.*, 1942, **75**, 308) claim to have prepared a 3 : 4-diol, b. p. 85°/0·4 mm., from the auto-oxidation products of (±)-menth-3-ene, and Tanaka (*J. Chem. Soc. Japan.*, 1932, **53**, 668; *Mem. Coll. Sci., Kyoto Univ.*, 1939, **22**, *A*, 97) obtained a glycol, m. p. 75—76°, when the hydrocarbon obtained by dehydration of (−)-menthol with alumina was oxidised by peracetic and perbenzoic acids and the oxides were hydrolysed : but the diols were not further characterised.

The properties of the glycols obtained in the present work are summarised in the Table.

Parent hydrocarbon	Glycol	M. p.	Di-*p*-nitrobenzoate, m. p.
(±)-*trans*-*p*-Menth-2-ene	(±)-*cis*-2-Hydroxymenthol	—	163°
	Glycol A	79°	168
	Glycol B	—	118
(±)-*cis*-*p*-Menth-2-ene	(±)-*cis*-2-Hydroxy*iso*menthol	—	138°
	Glycol C	78—78·5°	137
	Glycol D	69	152·3
	Glycol E	77	166

EXPERIMENTAL

(±)-trans-*Menth-2-ene*.—(±)-Menthyl toluene-*p*-sulphonate (70 g.) was added to a solution of sodium (23 g.) in dry ethanol (240 ml.), and the mixture heated on a steam-bath under reflux for 10 hours. Dilution with water (500 ml.) precipitated the crude menthene as an orange-coloured oil which was distilled with steam, and the hydrocarbon was extracted from the distillate with light petroleum (b. p. 40—60°). After drying ($MgSO_4$) it was fractionally distilled twice under partially reduced pressure in nitrogen, the second time over sodium. (±)-*trans*-Menth-2-ene was obtained as a fraction (19 g.), b. p. 69·5—70°/130 mm., d_4^{25} 0·8014, n_D^{25} 1·4480, $[R_L]_D$ 46·14 (Calc. 45·71). The substance proved to be explosive on attempted analysis.

Hydroxylation of (±)-trans-*Menth-2-ene with Osmium Tetroxide*.—Osmium tetroxide (1 g.) was dissolved in pure dry pyridine (0·6 g.)–benzene (25 ml.). After the addition of (±)-menth-2-ene (1 g., 100% excess) the yellow colour of the solution rapidly darkened to a dark brown. After being kept overnight at room temperature, the solvent was allowed to evaporate spontaneously, leaving a sticky brown residue which was shaken in chloroform with successive portions (30 ml.) of 1% aqueous potassium hydroxide containing mannitol (10%) until the alkali no longer acquired a pink colour and the chloroform solution appeared colourless. Removal of the solvent under reduced pressure left a brown viscous oil (0·6 g.). Attempts to purify the crude glycol by distillation and sublimation under reduced pressure and by chromatography on activated alumina were unsuccessful. The crude glycol gave a *di*-p-*nitrobenzoate* (pale yellow needles from methanol), m. p. 163° (Found : C, 61·0; H, 5·1; N, 6·0. $C_{24}H_{26}O_8N_2$ requires C, 61·3; H, 5·5; N, 6·1%).

Hydroxylation of (±)-trans-*Menth-2-ene with Peracetic Acid*.—Hydrogen peroxide (40 ml.; 30%) was added to acetic acid (160 ml.) and the mixture heated at 80° for 1 hour, and then cooled to 50°. (±)-*trans*-Menth-2-ene (14 g.) was added and the temperature maintained for 50 hours. The acid solution was poured into water (1 l.), extracted with benzene (4 × 50 ml.), and the extract washed successively with dilute sodium carbonate solution and water. Drying ($MgSO_4$) and removal of the solvent gave the mixed glycol monoacetates, which were hydrolysed forthwith under reflux for 2 hours with a solution of potassium hydroxide (12 g.) in water (30 ml.). Continuous extraction of the product with ether for 8 hours, drying ($MgSO_4$), and removal of the solvent gave the crude glycol (12 g.) as a pale yellow viscid oil.

(*a*) The crude glycol (12 g.) was distilled under reduced pressure and the fraction (10 g.), b. p. 109—111°/1·3 mm., collected. The distilled glycol was a colourless viscid oil which showed no tendency to crystallise. The distilled glycol (20 g.) was converted into the di-*p*-nitrobenzoate with *p*-nitrobenzoyl chloride (50 g.) in dry benzene (50 ml.)–pyridine (20 ml.). After 24 hours the esterification mixture was worked up. Crystallisation of the crude product from absolute alcohol gave an ester (21 g.), m. p. 164—167°. This was hydrolysed, without further purification, under reflux for 4 hours with a solution of potassium hydroxide (20 g.) in methanol (150 ml.). After dilution with water (150 ml.) the methanol was removed *in vacuo* and the residue was continuously extracted for 8 hours with light petroleum (75 ml.; b. p. 40—60°). Overnight the extract deposited *glycol A* (4·5 g.) as needles, m. p. 79°. Concentration of the mother-liquor and cooling to 0° produced a further quantity (1 g.) of the same material. Recrystallisation of the glycol several times from light petroleum (b. p. 40—60°) did not affect the m. p. (Found: C, 70·0; H, 11·9. $C_{10}H_{20}O_2$ requires C, 69·8; H, 11·6%). The pure glycol gave a *di*-p-*nitrobenzoate* (pale yellow plates from ethanol), m. p. 168° (Found: C, 61·4; H, 5·7; N, 6·1. $C_{24}H_{26}O_8N_2$ requires C, 61·3; H, 5·5; N, 6·0%). The pure ester (m. p. 168°) when mixed with the slightly impure ester (m. p. 164—167°) from which the glycol was regenerated caused no depression of m. p.

(*b*) The crude glycol (11 g.) from the hydroxylation of (±)-*trans*-menth-2-ene (14 g.) with peracetic acid was fractionally distilled through a short column of glass helices and three fractions were collected: (i) oil (1·1 g.), b. p. 90—100°/1·5 mm., (ii) viscous oil (5·7 g.), b. p. 105—108°/1·5 mm., (iii) viscous oil (3·5 g.), b. p. 112—114°/1·5 mm. Fractions (ii) and (iii) partly crystallised overnight after seeding with pure glycol from (*a*). Crystallisations of fraction (ii) from light petroleum (b. p. 40—60°) at −80° gave needles (2·1 g.), m. p. 76—78°, and (iii) also yielded the same product (0·8 g.). Recrystallisation of the combined samples from the same solvent gave pure glycol A (2·2 g.), m. p. 79°, identical with the product obtained in (*a*). The petroleum mother-liquors from the crystallisations of the glycol were combined and crude glycol was recovered (5·3 g.). Fractional distillation through a short column of glass helices gave fractions (iv) viscid oil (0·8 g.), b. p. 108—112°/0·7 mm., and (v) viscid oil (2·0 g.), b. p. 112°/0·7 mm. Distillation of the material washed from the helice column with ether gave (vi), a viscid oil (1·5 g.), b. p. 115°(bath)/0·1 mm. Distillation of the still residue from the fractionation gave (vii), a viscid oil (0·5 g.), b. p. 116—118°(bath)/0·1 mm. None of the distillates could be induced to crystallise. The last four samples were esterified separately with *p*-nitrobenzoyl chloride (25% excess) in pyridine at room temperature for 72 hours. Fractional crystallisation from absolute ethanol of the diesters from (iv), (v), and (vii) yielded only the diester of glycol A (m. p. 168°) previously described. The mother-liquors from the crystallisation of the same diester from (vi) slowly deposited a small quantity (250 mg.) of diester (long needles), m. p. 117°. Recrystallisation of this material from aqueous methanol gave a pure *diester* (of glycol B), m. p. 118° (Found: C, 61·4; H, 5·4; N, 6·1%).

(±)-cis-*Menth*-2-*ene*.—(±)-*iso*Menthyl toluene-*p*-sulphonate (m. p. 64°) (Hückel and Niggemeyer, *loc. cit.*) (88 g.) was converted into the hydrocarbon with a solution of sodium ethoxide in dry ethanol as described above for (±)-*trans*-menth-2-ene. The (±)-cis-*menth*-2-*ene* obtained (22 g.) had b. p. 68—68·5°/50 mm., d_4^{25} 0·8161, n_D^{25} 1·4519, $[R_L]_D$ 45·64 (Calc. 45·71) (Found: C, 86·4; H, 13·4. $C_{10}H_{18}$ requires C, 87·0; H, 13·0%).

Hydroxylation of (±)-cis-*Menth*-2-*ene with Osmium Tetroxide*.—The oxidation was carried out in benzene in the presence of pyridine as described above for (±)-*trans*-menth-2-ene. The dark brown addition complex partly crystallised from solution on storage. The crude (±)-*cis*-2-hydroxy*iso*menthol (0·4 g.) was obtained as a dark brown viscid oil from which the pure glycol could not be isolated. The crude product gave a *di*-p-*nitrobenzoate* which was readily obtained pure after two crystallisations from methanol, as small pale yellow prisms, m. p. 138° (Found: C, 61·7; H, 5·5; N, 6·4%).

Hydroxylation of (±)-cis-*Menth*-2-*ene with Peracetic Acid*.—(±)-*cis*-Menth-2-ene (13·8 g.) was hydroxylated with a dilute solution of peracetic acid, and the crude glycol isolated as described above for (±)-*trans*-menth-2-ene. In the present case the crude glycol was thrice extracted with ether (100 ml.) from the hydrolysis mixture instead of by continuous extraction. The crude glycol (9·6 g.) was a pale yellow viscid oil. Distillation of the crude glycol under reduced pressure gave fractions, (i) (0·3 g.) b. p. 72—74°/0·06 mm., (ii) a viscid oil (4·3 g.), b. p. 74—76°/0·06 mm., (iii) a pale yellow viscid oil (3·5 g.), b. p. 76—78°/0·06 mm. Small amounts (0·5 g.) of fractions (ii) and (iii) were separately esterified with *p*-nitrobenzoyl chloride (50% excess) in pyridine at room temperature for 48 hours. Attempted crystallisation of the crude esters from ethanol gave oils which gradually solidified. Slow recrystallisation (24 hours) gave in each case a mixture of two forms melting at 134—138° (prisms) and 164—166° (needles) respectively. Fractional crystallisation from ethanol of the combined products gave a *di*-p-*nitrobenzoate* (0·45 g.) (of glycol D), m. p. 152—153° (prisms from ethanol) (Found : C, 61·7; H, 5·6; N, 5·9%), and a *di*-p-*nitrobenzoate* (0·28 g.) (of glycol E), m. p. 166—167° (needles from ethanol) (Found : C, 61·7; H, 5·6; N, 6·0%). The ester of higher m. p. was the more soluble in ethanol.

The fractions (ii) and (iii) of the distilled glycol partly crystallised overnight. Fractional crystallisation of fraction (ii) (3·8 g.) from light petroleum (b. p. 40—60°) gave needles (0·22 g.), m. p. 78—78·5°, and plates (1·91 g.), m. p. 60—65°. Fraction (iii) similarly gave the needles (0·45 g.), m. p. 78—78·5°, and plates (1·5 g.), m. p. 60—65°. Recrystallisations of the material of m. p. 78—78·5° from light petroleum gave *glycol C*, m. p. 78—78·5°, which on admixture with the glycol A obtained from the hydroxylation of (±)-*trans*-menth-2-ene was depressed to 50—55° (Found : C, 70·1; H, 11·6. $C_{10}H_{20}O_2$ requires C, 69·8; H, 11·6%). Recrystallisation of the combined samples of glycol, m. p. 60—65° (3·4 g.), twice from light petroleum gave *glycol D* (2·0 g.), m. p. 69° (Found : C, 70·2; H, 11·3%).

Evaporation of the solvent from the mother-liquors from the crystallisations of the glycols left an oil (3·8 g.), which partly crystallised during several weeks. The crystals were drained on a tile, a process which owing to the high viscosity required several days. The crystals (2·5 g.) then had m. p. 55—65°. Three recrystallisations from light petroleum (b. p. 40—60°) gave glycol E (1·7 g.), m. p. 77°. A mixture of this material with glycol C melted at 52—60°, and one with glycol A melted at 43—49°. Glycol E (0·2 g.) with *p*-nitrobenzoyl chloride (0·5 g.) in pyridine (10 ml.) (48 hours at room temperature) gave a di-*p*-nitrobenzoate (pale yellow fine needles from ethanol), m. p. 166°, identical with the similar ester previously obtained from the crude glycol.

Glycol C gave a di-*p*-nitrobenzoate, m. p. 137° (pale yellow needles from ethanol) (Found : C, 61·7; H, 5·5; N, 6·1%).

Glycol D gave a di-*p*-nitrobenzoate, m. p. 152—153°, identical with the similar ester obtained from the crude glycol.

Hydroxylation of (±)-*Menth*-3-*ene with Peracetic Acid*.—The hydrocarbon (10 g.), b. p. 40—45°/1 mm., obtained as a by-product from the nitrous acid deamination of (±)-*iso*menthylamine, was treated with sodium (2 g.) and fractionated in nitrogen. The hydrocarbon obtained (7 g.), b. p. 43—44°/1 mm., was hydroxylated with a dilute solution of peracetic acid, and the pale yellow crude glycol (5·5 g.) isolated in the manner described above for (±)-*cis*-menth-2-ene. Fractional distillation gave fractions, (i) (1·2 g.), b. p. 85—106°/1 mm., (ii) (2·3 g.), b. p. 106—108°/1 mm., and (iii) a pale yellow viscid oil (1·5 g.), b. p. 106—108°/1 mm. Fractions (ii) and (iii) did not crystallise and were separately converted into the di-*p*-nitrobenzoate. Tedious fractional crystallisation from ethanol of the ester from fraction (ii) yielded glycol E di-*p*-nitrobenzoate (0·12 g.), m. p. 166°, identical with the product previously obtained, and glycol C di-*p*-nitrobenzoate (70 mg.), m. p. 137°; the crude ester from fraction (iii) yielded glycol E di-*p*-nitrobenzoate (70 mg.), m. p. 166°, and glycol D di-*p*-nitrobenzoate (60 mg.), m. p. 152—153°.

Catalytic Hydroxylation of (±)-trans-*Menth*-2-*ene*.—(±)-*trans*-Menth-2-ene (7 g.) was dissolved in the hydrogen peroxide–*tert*.-butanol reagent (Milas and Sussman, *loc. cit.*) (40 ml.) and cooled to 0°. Then was added an ice-cold solution of osmium tetroxide (0·1 g.) in the same solvent (10 ml.). The reaction was allowed to proceed at 0° for 72 hours. Removal of the butanol and unchanged hydrocarbon (3 g.) by distillation *in vacuo* left a dark oil, yielding (i) a slightly viscid oil (1·3 g.), b. p. 100—110°/0·5 mm., and (ii) a pale yellow viscid oil (1·2 g.), b. p. 110—120°/0·5 mm. Neither fraction crystallised nor could *p*-nitrobenzoates be obtained from them.

Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

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