706. p-*Menthane-2 : 3-diols. Part II.* Catalytic Hydrogenation of Diosphenol and Reduction by Sodium and Ethanol.*

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

Reinvestigation of the reduction of diosphenol by sodium and ethanol has confirmed the production of (±)-menthol and a mixture of stereoisomeric glycols. One of the diols previously obtained has been more fully characterised; and a second glycol has been isolated in a pure state. Catalytic hydrogenation of diosphenol at laboratory temperatures yields substantially only one glycol and it is related to (±)-*neoiso*menthol. The additional data now available enable tentative configurations to be assigned to most of the racemic *p*-menthane-2 : 3-diols.

A synthesis of diosphenol in good yield from menthone, through 2-hydroxymenthone, is described.

In Part I* a system of nomenclature for the eight stereoisomeric racemic *p*-menthane-2 : 3-diols was proposed, and the isolation of two glycols which were considered to be (±)-*cis*-2-hydroxymenthol and (±)-*cis*-2-hydroxy*iso*menthol was described. In addition, five other diols were isolated, but as configurations could not definitely be assigned to the compounds they were referred to as glycols A, B, C, D, and E. Further work now enables configurations to be suggested in most cases.

The reduction of diosphenol by Kondakov and Bachtschiev (*J. pr. Chem.*, 1901, **63**, 49) yielded (±)-menthol and a mixture from which a crystalline glycol, m. p. 92°, was obtained. This was later shown to be a *p*-menthane-2 : 3-diol (Semmler and McKenzie, *Ber.*, 1906,

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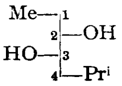
* Part I, Macbeth and Robertson, *J.*, 1953, 895.

39, 1160) as it gave α-methyl-α′-*iso*propyladipic acid on oxidation. Reduction of diosphenol with sodium and ethanol has now been shown to give a mixture of stereoisomeric glycols in yield of more than 60%. Fractional distillation of the viscid reduction product gave a forerun which contained (±)-menthol, and this was followed by a glycol fraction, a colourless very viscid oil which partly crystallised. Purification of the glycol itself, or through its di-*p*-nitrobenzoate, gave the pure diol, m. p. 91°, which is doubtless identical with that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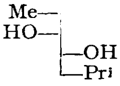
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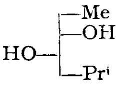
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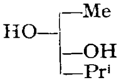
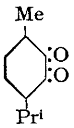

(IV)

previously prepared by Kondakov and Bachtschiev (*loc. cit.*). The di-*p*-nitrobenzoate, m. p. 118°, is identical with the similar ester of glycol B previously obtained by the per-acid hydroxylation of (±)-*trans*-*p*-menth-2-ene (see Part I, *loc. cit.*). On the basis of its preparation by the *trans*-hydroxylation of (±)-*trans*-*p*-menth-2-ene glycol B must have one of the configurations (I) or (II) : and in view of the fact that sodium and ethanol reduction of 2-alkyl*cyclo*hexanones gives essentially the *trans*-alcohol there is justification for concluding that the glycol, m. p. 91°, previously described as glycol B, is (±)-*trans*-2-hydroxymenthol (I) rather than (±)-*trans*-2-hydroxy*neo*menthol (II). The latter configuration is consequently assigned to glycol A, m. p. 79°, the other of the pair of diols obtained by the *trans*-hydroxylation of (±)-*trans*-*p*-menth-2-ene.

The syrup recovered after the separation of (±)-*trans*-2-hydroxymenthol was converted into the di-*p*-nitrobenzoate, and a pure ester, m. p. 166°, was obtained by fractional crystallisation from ethanol. This was found to be identical with the previously described di-*p*-nitrobenzoate from glycol E, and on hydrolysis gave a diol, m. p. 77°, which showed no depression on admixture with glycol E itself. As the latter was obtained by per-acid *trans*-hydroxylation of *cis*-*p*-menth-2-ene, it has either of the configurations (III) or (IV); and as it is obtained by the sodium and ethanol reduction of diosphenol it is concluded that glycol E is (±)-*trans*-2-hydroxy*iso*menthol (III). The alternative configuration (IV) is accordingly assigned to one of the other diols obtained in the *trans*-hydroxylation of *cis*-*p*-menth-2-ene, and glycol D, m. p. 69°, is believed to be (±)-*trans*-2-hydroxy*neoiso*menthol. This is necessarily tentative, as three glycols were obtained in the per-acid hydroxylation one of which (glycol C) was believed to be a 3 : 4-diol derived from *p*-menth-3-ene present as an impurity.

The assumptions that glycol B is *trans*-2-hydroxymenthol (I) and that glycol E is *trans*-2-hydroxy*iso*menthol (III) receive some support from the fact that sodium and ethanol reductions of piperitone, menthone, and *iso*menthone give rise to menthol and *iso*menthol (Read and Cook, *J.*, 1925, **127**, 2784; Hughesdon, Read, and Smith, *J.*, 1923, **123**, 2918). The similarity between the formulæ for diosphenol (V*a*, V*b*), pipertone (VI), menthone (VII), and *iso*menthone (VIII) suggests that under the same conditions their reductions might well follow similar stereochemical paths.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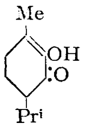
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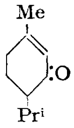
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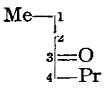
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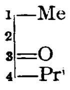
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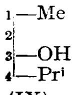
Catalytic hydrogenation of diosphenol by previous workers (Walker and Read, *J.*, 1934, 238; Cusmano and Boccucci, *Gazzetta*, 1923, **53**, 649) yielded mainly keto-alcohols, and no glycol appears to have been definitely isolated as a reaction product. Good yields of glycol have now been obtained by the hydrogenation in glacial acetic acid containing a trace of hydrogen chloride, when the reaction is carried out in the presence of Adams's platinum oxide catalyst at room temperature and a pressure of 30 atm. Fractionation of the product gave an appreciable amount of hydrocarbon and a glycol fraction which apparently contained only one diol. Crystallisation from light petroleum (b. p. 40—60°) gave the pure glycol, m. p. 76°, the di-*p*-nitrobenzoate of which melted at 147—148°. The same glycol was obtained from diosphenol by hydrogenation in ethanol solution at room temperature and 80 atm., Raney nickel (Pavlic and Adkins, *J. Amer. Chem. Soc.*, 1946, **68**, 1471) being used as catalyst. The glycol gave a monotoluene-*p*-sulphonate, m. p. 128°, which on reduction by lithium aluminium hydride (Schmid and Karrer, *Helv. Chim. Acta*, 1949, **32**, 1371) gave an oil possessing a strong menthol odour from which (±)-*neoiso*menthyl 3 : 5-dinitrobenzoate, m. p. 73°, was prepared. The *p*-nitrobenzoate could not be purified directly to a higher m. p. than 55°, a behaviour in accordance with Read and Grubb's observation (*J.*, 1934, 313).



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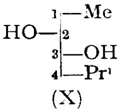
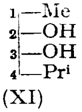


(X)



(XI)

The configuration of the glycol at $C_{(1)}$, $C_{(3)}$, and $C_{(4)}$ is fixed by its relationship with (±)-*neoiso*menthol (IX) and of the two possible configurations (X, XI) the latter [(±)-*cis*-2-hydroxy*neoiso*menthol] is preferred since the glycol did not appear as a product of the *trans*-hydroxylation of (±)-*cis*-menth-2-ene. The alternative configuration [(±)-*trans*-2-hydroxy*neoiso*menthol] has already been assigned to glycol D.

Although all the glycols examined readily yielded di-*p*-nitrobenzoates, only the (±)-*trans*-2 hydroxy*neo*menthol (m. p. 79°) gave a bis-3 : 5-dinitrobenzoate when esterified by normal methods. In the other cases the esters were obtained on heating the glycols under reflux for 30 min. with the acid chloride in benzene solution containing pyridine and leaving the mixture overnight. The esters were purified by crystallisation from benzene and light petroleum, and in some cases contained benzene of crystallisation. The bis-3 : 5-dinitrobenzoates of (±)-*cis*- and (±)-*trans*-2-hydroxy*neoiso*menthol contained two molecules of benzene of crystallisation which were readily lost at 80°. The ester of (±)-*trans*-2-hydroxymenthol contained one molecule of benzene which was released only on fusion, and glycol C, believed to be a 3 : 4-diol, behaved similarly.

Present views on the *p*-menthane-2 : 3-diols are summarised below.

Diol	M. p.	M. p. of di-*p*-nitrobenzoate	M. p. of bis-3 : 5-dinitrobenzoate
(±)-*cis*-2-Hydroxymenthol	—	163°	—
(±)-*trans*-2-Hydroxymenthol (B)	91°	118	218°
(±)-*cis*-2-Hydroxy*neo*menthol	—	—	—
(±)-*trans*-2-Hydroxy*neo*menthol (A)	79	168	173
(±)-*cis*-2-Hydroxy*iso*menthol	—	138	—
(±)-*trans*-2-Hydroxy*iso*menthol (E)	77	166	122
(±)-*cis*-2-Hydroxy*neoiso*menthol	76	147—148	82—83
(±)-*trans*-2-Hydroxy*neoiso*menthol (D)	69	152—153	65

The diosphenol initially used in the work was obtained by purification of a commercial sample of buchucamphor but, as the supply was limited, methods of preparing the substance were examined. Wallach (*Annalen*, 1924, **437**, 172) claimed to have obtained good yields of diosphenol by permanganate oxidation of piperitone, but subsequent workers (Düker, *J. pr. Chem.*, 1931, **129**, 145; Roberts, *J.*, 1915, **107**, 1466) did not find the method suitable, and in our hands yields of some 5% only were experienced. Nor did we find the oxidation of menthone by ferric chloride (Asahina and Mituhori, *J. Pharm. Soc. Japan*, 1922, **482**, 255; Asahina and Kuwada, *ibid.*, 1923, **491**, 1) or by selenium dioxide (Riley, Morley, and Friend, *J.*, 1932, 1875) satisfactory. Triebs and Bast's observation (*Annalen*, 1949, **561**, 165) that the action of meruric acetate on cyclic ketones gives rise to α-acetoxy-ketones, and in particular that 2-acetoxymenthone may be so derived, suggested that the oxidation of the 2-hydroxymenthone thus available might prove a suitable route to diosphenol. The use of bismuth oxide as a specific oxidising agent for acyloins to 1 : 2-diketones (Rigby, *J.*, 1951, 793) has proved satisfactory for the oxidation of 2-hydroxymenthone to diosphenol in yields approaching 50% on the menthone used.

EXPERIMENTAL

Diosphenol.—(*a*) A commercial sample of buchucamphor was distilled (b. p. 96—100°/10 mm.) and crystallised once from light petroleum (b. p. 40—60°). The purified diosphenol had m. p. 82°.

(*b*) *From menthone*. (−)-Menthone (15 g.) in glacial acetic acid (25 ml.) was heated with mercuric acetate (32 g.) at 130° until the crystalline mass which first formed had decomposed and precipitation of mercury was complete (2 hr.). Next morning the supernatant solution of 2-acetoxymenthone was decanted from the mercury and poured into water (400 ml.). After extraction with ether (150 ml.), drying ($MgSO_4$), and removal of the solvent by distillation, fractional distillation gave (i) unchanged menthone (3·5 g.), b. p. 55—60°/0·4 mm., and (ii) 2-acetoxymenthone (13·6 g., 77% on menthone used), b. p. 91—95°/0·4 mm. The 2-acetoxymenthone was obtained as a very pale yellow oil. A residue (0·8 g.) of viscid red oil remained after the distillation. 2-Acetoxymenthone (18 g.) was hydrolysed under reflux with a solution of potassium hydroxide (150 ml., 8%) for 20 min. The product was extracted with ether (100 ml.) and dried ($MgSO_4$), and the solvent removed by distillation. The residual 2-hydroxymenthone (12·2 g., 85%) was oxidised as follows without further purification.

2-Hydroxymenthone (12 g.) and bismuth oxide (15 g.) were heated in glacial acetic acid (40 ml.) at 110° for 2 hr. with constant agitation. After removal of the bismuth by filtration, the filtrate was poured into water (600 ml.). The product was extracted with ether (100 ml.) and the extract washed twice with aqueous sodium carbonate (5%, 50 ml., 50 ml.), then with water (50 ml.), and dried ($MgSO_4$). Removal of the solvent by distillation gave a residue which mostly crystallised but contained a small amount of yellow oil. Crystallisation of the residue from light petroleum (b. p. 40—60°) (cooled in the refrigerator) gave diosphenol (7·8 g., 73%), m. p. 82°. A mixture with an authentic sample (m. p. 82°) had m. p. 82°. The overall yield of diosphenol from menthone was 48%.

Reduction of Diosphenol with Sodium and Alcohol.—(*a*) Diosphenol (7 g.) was reduced in ethanol (125 ml.) with sodium (15 g.). After the addition of sodium was complete a further 50 ml. of ethanol was added, and the solution heated under reflux for 15 min. After cooling and dilution with water (200 ml.), ethanol was removed by distillation under partially reduced pressure. The product was continuously extracted (8 hr.) with light petroleum (b. p. 40—60°). No crystallisation from the petroleum solution (50 ml.) could be induced on cooling (finally to −80°). The solvent was removed by distillation, and the residue of crude glycol distilled under reduced pressure, yielding two fractions : (i) colourless oil (1·9 g.), b. p. 88—92°/1 mm., (ii) colourless viscid oil (4·3 g.), b. p. 118—120°/1 mm. Fraction (ii) partially crystallised. The crystals were separated from the oil by filtration and recrystallised from light petroleum, giving colourless needles (0·1 g.), m. p. 86—87°.

(*b*) Diosphenol (10 g.) was reduced with sodium (20 g.) in ethanol (200 ml.) as in (*a*). Fractionation of the crude product gave three fractions : (i) colourless oil with menthol odour (1·6 g.), b. p. 80—90°/0·8 mm., (ii) colourless, viscid oil (1·1 g.), b. p. 110—112°/0·8 mm., and (iii) colourless, very viscid oil (5·0 g.), b. p. 112—116°/0·8 mm.

Esterification of fraction (i) from (*b*) with *p*-nitrobenzoyl chloride (4 g.) in benzene (15 ml.) and pyridine (10 ml.) at room temperature for 24 hr. gave a crude ester (1·5 g.) from which was isolated by four recrystallisations from light petroleum (b. p. 40—60°) (±)-menthyl *p*-nitrobenzoate (0·25 g.), m. p. 91° (Found : C, 67·2; H, 7·5; N, 4·9. Calc. for $C_{17}H_{23}O_4N$: C, 66·9; H, 7·5; N, 4·6%). A mixture of this ester with an authentic sample of (±)-menthyl *p*-nitrobenzoate (m. p. 91°) melted at 91°.

Fraction (iii) from (*b*) partly crystallised slowly (several weeks) but was too viscous for filtration. Attempts to recrystallise the partly crystalline material from light petroleum (b. p. 40—60°) were unsuccessful. After removal of the solvent the remaining oil was combined with the remainder of fraction (ii) from (*a*) and refractionated, giving two fractions : (*a*) colourless, viscid oil (0·8 g.), b. p. 120—122°/7 mm., and (*b*) colourless, very viscid oil, b. p. 130—134°/7 mm. Fraction (*a*) was esterified with *p*-nitrobenzoyl chloride (2 g.) in benzene (15 ml.) and pyridine (15 ml.) at room temperature for 4 days. The product could not be crystallised satisfactorily. Crystallisation of fraction (*b*) from light petroleum (b. p. 40—60°) gave a crystalline glycol (1·5 g.), m. p. 86—88°. Two recrystallisations from light petroleum gave pure (±)-trans-2-*hydroxymenthol* (0·8 g.), m. p. 91° (Found : C, 70·0; H, 11·8. $C_{10}H_{20}O_2$ requires C, 69·8; H, 11·6%); the di-*p*-nitrobenzoate (Found : C, 61·7; H, 5·7; N, 6·2. Calc. for $C_{24}H_{26}O_8N_2$: C, 61·3; H, 5·5; N, 6·0%) had m. p. 118°, unchanged on admixture with a sample of the di-*p*-nitrobenzoate (m. p. 118°) obtained from the product of hydroxylation of (±)-*trans*-menth-2-ene (Macbeth and Robertson, *loc. cit.*) with per-acetic acid.

(±)-trans-2-*Hydroxy*iso*menthol from the Sodium and Alcohol Reduction Product.*—The oil (4·7 g.) recovered from the mother-liquors accumulated during the purification of (±)-*trans*-2-hydroxymenthol was esterified with *p*-nitrobenzoyl chloride (13·8 g.) in pyridine (40 ml.) at room temperature for 4 days. The crude ester was obtained as a yellow oil (11·7 g.). Attempted crystallisation of the oil from methanol gave an oil. The mother-liquor slowly deposited pale yellow needles (0·52 g.), m. p. 160—162°. Crystallisation of the oil gave a further crop (0·96 g.), m. p. 158—162°. Further evaporation of the mother-liquor gave more crystalline material (2·47 g.), m. p. 155—160° with noticeable softening at 112—117°. Still further evaporation gave 2·6 g., m. p. 105—112° with marked softening at 85—90°. Attempts to isolate more crystalline material from the mother-liquors yielded only oils. Recrystallisation of the two fractions of higher m. p. from ethanol gave a di-*p*-nitrobenzoate (pale yellow needles), m. p. 166° (0·83 g.), identical with the di-*p*-nitrobenzoate of glycol E obtained from the hydroxylation of (±)-*cis*-menth-2-ene (Macbeth and Robertson, *loc. cit.*). This is now regarded as (±)-*trans*-2-hydroxy*iso*menthol.

(±)-*trans*-2-Hydroxy*iso*menthol di-*p*-nitrobenzoate (800 mg.) was hydrolysed under reflux for 2 hr. in methanol (12 ml.) containing potassium hydroxide (0·5 g.). After dilution with water (20 ml.) the methanol was removed by distillation. The glycol (200 mg.) crystallised from the aqueous liquor as fine colourless needles, m. p. 74—76°. One recrystallisation from light petroleum (b. p. <40°) gave pure (±)-*trans*-2-hydroxy*iso*menthol, m. p. 77°. Mixtures of the product with (±)-*cis*-2-hydroxy*neoiso*menthol (m. p. 76°), (±)-*trans*-2-hydroxy*neo*menthol (m. p. 79°), or glycol C (m. p. 78—78·5°) all melted within the range 35—45°. The m. p. was not depressed on admixture with the glycol E [(±)-*trans*-2-hydroxy*iso*menthol, m. p. 77°] obtained by per-acid hydroxylation of (±)-*cis*-menth-2-ene.

The two ester fractions of lower m. p. obtained from the crystallisation of the crude di-*p*-nitrobenzoate probably consisted of mixtures of (±)-menthyl *p*-nitrobenzoate and the di-*p*-nitrobenzoates of (±)-*trans*-2-hydroxymenthol and of (±)-*trans*-2-hydroxy*iso*menthol and could not be purified satisfactorily by recrystallisation.

Hydrogenation of Diosphenol over Raney Nickel.—Diosphenol (7 g.) was suspended in ethanol (10 ml.) and hydrogenated during 2·5 hr. at room temperature 1200 lb./sq. in over Raney nickel. (0·5 g.). The hydrogenated solution was filtered and diluted with water (25 ml.). The alcohol was removed by distillation, and the product extracted continuously from the residue for 4 hr. with light petroleum (b. p. 40—60°). The extract was reddish. The petroleum extract was concentrated to 15 ml. The glycol crystallised from the solvent during 2 days at room temperature. The crystalline glycol obtained (2·1 g.) had m. p. 75—76°. On further evaporation the mother-liquor yielded an additional quantity of glycol (1·5 g.), m. p. 68—72°. Recrystallisation of this second crop gave 0·9 g., m. p. 75—76°. Recrystallisation of all the glycol, m. p. 75—76° (3·0 g.), gave pure (±)-cis-2-*hydroxy*neoiso*menthol* as needles (from light petroleum) (2·0 g.), m. p. 76° (Found: C, 69·8; H, 11·4. $C_{10}H_{20}O_2$ requires C, 69·8; H, 11·6%); *di*-p-*nitrobenzoate*, m. p. 148° (Found: C, 61·5; H, 5·8; N, 6·0. $C_{24}H_{26}O_8N_2$ requires C, 61·3; H, 5·5; N, 6·0%). Admixture with (±)-*trans*-2-hydroxy*neo*menthol (m. p. 79°) and with (±)-*trans*-2-hydroxy*iso*menthol (m. p. 77°) depressed the m. p. to 30—40° and to 45—50°, respectively. The di-*p*-nitrobenzoate (m. p. 148°) of (±)-*cis*-2-hydroxy*neoiso*menthol when admixed with the di-*p*-nitrobenzoate (m. p. 152—153°) of (±)-*trans*-2-hydroxy*neoiso*menthol melted at 135—140°.

Hydrogenation of Diosphenol over Adams's Catalyst.—Diosphenol (10 g.) was suspended in glacial acetic acid (30 ml.). After the addition of concentrated hydrochloric acid (1 drop) the mixture was hydrogenated over platinum oxide (200 mg.) during 1 hr. at 25°/400 lb./sq. in. The solution was filtered and poured into water (500 ml.). The product was extracted with ether (100 ml.), and the ethereal solution washed with water (100 ml.), 5% sodium carbonate solution (100 ml.), and again with water (100 ml.). After drying ($MgSO_4$), the solvent was removed from the extract by distillation. Crystallisation of the colourless residue (8·6 g.) from light petroleum (b. p. 40—60°) gave (±)-*cis*-2-hydroxy*neoiso*menthol (4·5 g.), m. p. 75—76°. One recrystallisation from light petroleum raised the m. p. to 76°. The product was identical with that obtained by hydrogenation of diosphenol over Raney nickel and gave the same di-*p*-nitrobenzoate, m. p. 147—148°.

Careful fractionation of the material recovered from the mother-liquors from the purification of the glycol from several such preparations gave a large range of fractions whose b. p.s ranged from 58°/1 mm. to 95°/1 mm. Their compositions were not determined. A glycol fraction, b.p. 98—100°, amounting to 15% of the total material (14·2 g.) fractionated, was obtained. From this only (±)-*cis*-2-hydroxy*neoiso*menthol (m. p. 76°) could be obtained by crystallisation from light petroleum (b. p. 40—60°).

Monotoluene-p-*sulphonate of* (±)-cis-2-*Hydroxy*neoiso*menthol*.—(±)-*cis*-2-Hydroxy*neoiso*menthol (0·86 g.) was esterified with toluene-*p*-sulphonyl chloride (2·5 g.) in pyridine (7 ml.) during 24 hr. at room temperature. Crystallisation of the crude product from aqueous methanol gave colourless leaflets, m. p. 126—127°. Recrystallisation from aqueous methanol gave the pure *monotoluene*-p-*sulphonate*, m. p. 128° (Found : C, 62·6; H, 7·9; S, 9·7. $C_{17}H_{26}O_4S$ requires C, 62·6; H, 8·0; S, 9·8%).

(±)-neoiso*Menthol*.—The monotoluene-*p*-sulphonate (400 mg.) was heated under reflux with lithium aluminium hydride (30 mg.) in dry ether during 24 hr. The excess of lithium aluminium hydride was decomposed with water, and the white precipitate dissolved by addition of 2N-sulphuric acid. After being washed with 2N-sodium hydroxide (15 ml.) and water (15 ml.), the ethereal solution was dried ($MgSO_4$) and the solvent removed, leaving a colourless oil (200 mg.). Esterification as above gave (±)-*neoiso*menthyl *p*-nitrobenzoate (yellow leaflets from light petroleum), m. p. 55—56°. Esterification with 3 : 5-dinitrobenzoyl chloride gave (±)-*neoiso*menthyl 3 : 5-dinitrobenzoate, m. p. 73°.

Bis-3 : 5-*dinitrobenzoates*.—(*a*) (±)-*trans*-2-Hydroxy*neo*menthol (200 mg.) was esterified with 3 : 5-dinitrobenzoyl chloride in pyridine in the usual way. Crystallisation of the crude ester from ethanol gave (±)-trans-2-*hydroxy*neo*menthol bis*-3 : 5-*dinitrobenzoate* as small, pale yellow rosettes, m. p. 173° (Found : C, 51·7; H, 4·5; N, 10·0. $C_{24}H_{24}O_{12}N_4$ requires C, 51·4; H, 4·3; N, 10·0%).

(*b*) In all other cases the bis-3 : 5-dinitrobenzoates were prepared by boiling the glycol (100—200 mg.) and 3 : 5-dinitrobenzoyl chloride (300—600 mg.) under reflux in benzene (12 ml.) and pyridine (3 ml.) for 0·5 hr. and keeping the mixture at room temperature overnight. The crude esters were crystallised from mixtures of benzene and light petroleum, with the following results :

(i) (±)-*trans*-2-Hydroxymenthol (m. p. 91°) gave the corresponding *bis*-3 : 5-*dinitrobenzoate* as pale yellow needles, m. p. 218°, containing 1 molecule of benzene of crystallisation (Found : C, 55·5; H, 4·5; N, 8·8. $C_{24}H_{24}O_{12}N_4,C_6H_6$ requires C, 55·6; H, 4·6; N, 8·8%). The benzene of crystallisation could be removed only by fusion of the ester (Found, for unsolvated *ester* : C, 51·5; H, 4·3; N, 10·3. $C_{24}H_{24}O_{12}N_4$ requires C, 51·4; H, 4·3; N, 10·0%).

(ii) (±)-*trans*-2-Hydroxy*iso*menthol (m. p. 77°) gave the corresponding *bis*-3 : 5-*dinitrobenzoate* as pale yellow, unsolvated needles, m. p. 122°, containing no benzene of crystallisation (Found : C, 51·5; H, 4·3; N, 10·0%).

(iii) (±)-*trans*-2-Hydroxy*neoiso*menthol (m. p. 69°) gave a *bis*-3 : 5-*dinitrobenzoate* as pale yellow, transparent leaflets, m. p. 65°, containing two molecules of benzene of crystallisation. Heating the freshly crystallised ester (61·8 mg.) for 2 hr. at 100° under reduced pressure (0·1 mm.) caused a loss in weight of 21·7% (13·4 mg.) ($C_{24}H_{24}O_{12}N_4,2C_6H_6$ requires $2C_6H_6$, 21·8%). The residue (48·4 mg.) of desolvated *ester* was obtained as a glass with an indefinite m. p. 70—75° (Found : C, 51·8; H, 4·3; N, 9·8%). When kept for several days the freshly crystallised ester lost one molecule of benzene, the *monosolvate* having an opaque powdery appearance (Found : C, 55·7; H, 4·5; N, 8·8%).

(iv) Glycol C (m. p. 78—78·5°) gave a monosolvated *bis*-3 : 5-*dinitrobenzoate* as pale yellow needles, m. p. 185° (Found : C, 55·9; H, 4·6; N, 9·2%). The benzene of crystallisation could be removed only by fusion of the ester for several minutes (Found, for unsolvated *ester* : C, 51·6; H, 4·5; N, 9·9%).

(v) (±)-*cis*-2-Hydroxy*neoiso*menthol gave a disolvated *bis*-3 : 5-*dinitrobenzoate* as pale yellow prisms, m. p. 81—83° (Found : C, 60·6; H, 5·1; N, 7·5. $C_{36}H_{36}O_{12}N_4$ requires C, 60·5; H, 5·0; N, 7·8%). A small sample (101·2 mg.) of the ester heated under reduced pressure (0·1 mm.) for 2 hr. at 80° and a further 1 hr. at 110° underwent a loss in weight of 21·4% (21·6 mg.) ($2C_6H_6$ requires 21·8%) giving the pure *ester*, m. p. 169° (Found : C, 51·7; H, 4·5; N, 9·9%).

(vi) Attempts to prepare bis-3 : 5-dinitrobenzoates from (±)-*cis*-2-hydroxymenthol and from (±)-*cis*-2-hydroxy*iso*menthol failed.

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