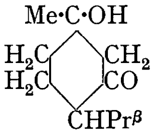
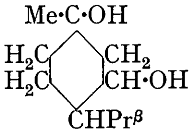
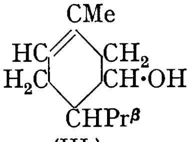
41. *Researches in the Menthone Series. Part XIV.* dl-1-*Hydroxymenthone,* dl-*Menthane*-1 : 3-*diols, and* dl-Δ^6-neo*Menthen*-3-*ol.*

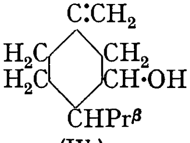
By John Read and Geoffrey Swann.

Its resistance to oxidation by Beckmann's reagent, as noted below, indicates that the *dl*-hydroxymenthone resulting from the catalytic hydrogenation of *dl*-piperitone oxide (Walker and Read, J., 1934, 241) is *dl*-1-hydroxymenthone (I): the alternative 2-hydroxymenthone would yield diosphenol in this way. Further hydrogenation of this substance furnished a mixture of dl-*menthane*-1 : 3-*diols* (II), of which four stereoisomeric *dl*-forms are possible. One of these, m. p. 143°, has been isolated and characterised by means of its 3 : 5-dinitrobenzoate, m. p. 199—200.°


(I.)


(II.)


(III.)


(IV.)

Dehydration of the mixture of diols yielded an unsaturated menthen-3-ol, which was converted by hydrogenation into a mixture of menthols. One of these was identified as *dl-neo*menthol, and the other was therefore *dl-neoiso*menthol (Read and Grubb, J., 1934, 1779). Consequently, the menthenol in question belonged to the *neo*-series, with *cis*-H atoms in positions 3 and 4. From its method of formation, this menthenol must be Δ^1, Δ^6, or $\Delta^{1(7)}$. It showed none of the characteristic properties of Δ^1-menthen-3-ol (piperitols; see J., 1930, 2770; 1934, 308), and it resisted oxidation with Beckmann's reagent; it displayed no marked exaltation of molecular refractivity, characteristic of a semicyclic double bond; moreover, upon ozonisation it furnished only a little formaldehyde. Thus the alcohol was apparently dl-Δ^6-neo*menthen*-3-*ol* (III), with possibly a small amount of $\Delta^{1(7)}$-*neo*menthen-3-ol (IV), into which it may conceivably isomerise under favourable conditions.

Little, if anything, seems to be known of βγ-unsaturated alicyclic alcohols, and further investigations will be necessary in order to determine whether reluctant oxidation to the corresponding ketone is a characteristic of the type. Incidentally, the Δ^6-menthen-3-one obtained in an impure condition from this alcohol appears to be the first known example of a monocyclic terpene ketone with an endocyclic double bond which is not in the αβ-position.

Experimental.

dl-1-*Hydroxymenthone*.—This substance was prepared by the catalytic hydrogenation of *dl*-piperitone oxide, either by the method of Walker and Read (J., 1934, 241) or in presence of other suitable low-temperature catalysts. It crystallised in colourless prisms, m. p. 89—90°. The faces of the crystals were too dull and uneven to permit of goniometric characterisation. Prof. H. L. Bowman, Department of Mineralogy, University of Oxford, reported that they were probably orthorhombic: " a combination of a bipyramid with two pinakoid forms, resembling the rhombic dodecahedron, but one of the pinakoids has nearly square faces. The optic axial plane is parallel to the square pinakoid faces, and the negative acute bisectrix is normal to the other pinakoid. There are no faces present which would throw any light on the question of enantiomorphism."

dl-1-Hydroxymenthone resisted oxidation with Beckmann's reagent (*Annalen*, 1889, **250**, 335). When heated with its own weight of potassium bisulphate at 135° for 30 minutes, it yielded *dl*-piperitone; also when heated on the water-bath in aqueous alcoholic solution with the acetate of hydroxylamine or semicarbazide, it yielded, respectively, the oxime and semicarbazone of *dl*-piperitone. The *semicarbazone*, prepared in cold aqueous alcohol, formed long, colourless needles, m. p. 190—190·5° (Found: C, 58·3; H, 9·3. $C_{11}H_{21}O_2N_3$ requires C, 58·1; H, 9·3%). The crude oxime, prepared similarly, melted at 94—98°, and was too soluble to permit of fractional recrystallisation. The p-*nitrobenzoate* crystallised from methyl alcohol in yellow needles, m. p. 109° (Found: C, 63·9; H, 6·7. $C_{17}H_{21}O_5N$ requires C, 63·9; H, 6·6%). The *l*-menthoxyacetate was a syrup.

dl-*Menthane*-1 : 3-*diols*.—In presence of suitable catalysts at about 7 atm. pressure it proved possible to hydrogenate *dl*-piperitone oxide either to the above *dl*-1-hydroxymenthone (at 30—

35°) or to continue to the diol stage (at 65°), with the respective uptake of 2 or 4 hydrogen atoms per molecule. The second fraction obtained upon distilling the product of the complete hydrogenation formed a very viscid, odourless oil, b. p. 129—138°/12·5 mm., $n_D^{19°}$ 1·4730 (Found : C, 69·8; H, 11·5. $C_{10}H_{20}O_2$ requires C, 69·3; H, 11·6%). When treated in pyridine with *p*-nitro- or 3 : 5-dinitro-benzoyl chloride (1 or 2 mols.), this mixture of *diols* yielded syrupy or vitreous products. A *monoacetate* was obtained similarly as a thick oil, b. p. 130—136°/17 mm., $n_D^{18°}$ 1·4585 (Found : C, 67·3; H, 10·4. $C_{12}H_{22}O_3$ requires C, 67·3; H, 10·3%). Beckmann's reagent oxidised the mixture of diols to the above *dl*-1-hydroxymenthone, m. p. 89—90°.

The product obtained by the catalytic hydrogenation of purified *dl*-1-hydroxymenthone crystallised partly when kept. When it was washed with ether–light petroleum and recrystallised five times from acetone, a homogeneous dl-*menthan*-1 : 3-*diol* separated in small colourless crystals, m. p. 143° (Found : C, 70·1; H, 11·6%).

The crystalline diol reacted with *p*-nitrobenzoyl chloride to form a glass, but the 3 : 5-*dinitrobenzoate* separated from methyl alcohol in yellow prisms, m. p. 199—200° (decomp.) (Found : C, 51·7; H, 4·3. $C_{24}H_{24}O_{12}N_4$ requires C, 51·4; H, 4·3%).

dl-Δ^6-neo*Menthen*-3-*ol*.—The above mixture of diols was heated with its own weight of potassium bisulphate at 140° for 30 minutes : the product yielded about 15% of a terpene fraction and 45% of an alcohol fraction, when distilled, the remainder being unchanged diol. Treatment with 20% aqueous oxalic acid on a boiling water-bath for 2 hours was preferred, as it gave about 25% of terpene (b. p. to 99°/12 mm., $n_D^{16°}$ 1·4691) and 45% of alcohol. The latter fraction had b. p. 99—104°/12 mm., 100—108°/19 mm., $n_D^{16°}$ 1·4750, $n_D^{19°}$ 1·4724. Unsatisfactory results were obtained by heating the diol with anhydrous copper sulphate in ligroin, *d*-camphor-10-sulphonic acid in dry benzene, or acetic anhydride. When the alcohol fraction was esterified in dry pyridine with 3 : 5-dinitrobenzoyl chloride, it gave a 60% yield of crude ester; upon fractional recrystallisation from methyl alcohol–ethyl acetate (3 : 1), about one-third of this was obtained in yellow prisms, m. p. 118—119° (Found : C, 58·8; H, 5·8. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·8%). The dl-Δ^6-neo*menthen*-3-*yl* 3 : 5-*dinitrobenzoate* so prepared was readily hydrolysed when heated under reflux with 2·5% methyl-alcoholic potassium hydroxide. The resulting dl-Δ^6-neo*menthen*-3-*ol* was a colourless, odourless, mobile oil, b. p. 99°/17·5 mm., $n_D^{15°}$ 1·4792, $n_D^{18°}$ 1·4783, $d_{4°}^{15°}$ 0·9346, $[R_L]_D$ 46·78 (calc. for $C_{10}H_{18}O$, 1 $|^{=}$, 47·2). Another specimen had $n_D^{15°}$ 1·4800, $d_{4°}^{15°}$ 0·9343, $[R_L]_D$ 46·94 (Found : C, 77·4; H, 11·4. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). The *p*-nitrobenzoate was a white, micro-crystalline powder, m. p. 82—83°; it was phototropic and became yellow when exposed to bright light. The *d*-camphor-10-sulphonate was too soluble to permit of recrystallisation.

Upon hydrogenation at room temperature in methyl alcohol containing a 2% palladised calcium carbonate catalyst (compare J., 1934, 241), the above menthenol yielded an oil smelling of menthol. The derived 3 : 5-dinitrobenzoate, after several recrystallisations from methyl alcohol, furnished a fraction consisting of pale yellow needles, m. p. 129—130°. Mixtures of this substance with *dl-iso*menthyl 3 : 5-dinitrobenzoate (m. p. 130°) and *dl-neo*menthyl 3 : 5-dinitrobenzoate (m. p. 130°; J., 1933, 170) melted at 112° and 130°, respectively : the substance was thus *dl-neo*menthyl 3 : 5-dinitrobenzoate.

When oxidised with Beckmann's reagent under widely varied conditions, the menthenol yielded products which, although partly ketonic, appeared to vary in composition. In an oxidation conducted below 75°, the black chromium compound broke up only partially, and yielded a yellow oil with a strong odour, b. p. 93—95°/17 mm., $n_D^{17°}$ 1·4711. The derived *semicarbazone* was not homogeneous : a purified specimen crystallised from methyl alcohol in yellow prisms, m. p. 179—180° (Found : C, 63·4; H, 9·0. $C_{11}H_{19}ON_3$ requires C, 63·2; H, 9·1%). Another fraction of semicarbazone consisted of a white powder, m. p. *ca.* 200°. The oxime was a viscid syrup. Chromic anhydride in glacial acetic acid and potassium permanganate in acetone failed to oxidise the menthenol. Upon oxidation with 5% aqueous alkaline potassium permanganate (compare Simonsen, J., 1921, **119**, 1653), the menthenol gave rise to an acidic product consisting of a thick brown oil which would not crystallise even after fractional distillation in a vacuum; neither formaldehyde nor formic acid was detected among the oxidation products.

An ozonisation of the above *dl*-Δ^6-*neo*menthen-3-yl 3 : 5-dinitrobenzoate, m. p. 118—119°, which was kindly undertaken for us by Prof. J. L. Simonsen, F.R.S., gave only a small quantity of formaldehyde, and decomposition of the ozonide yielded very little neutral product.

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