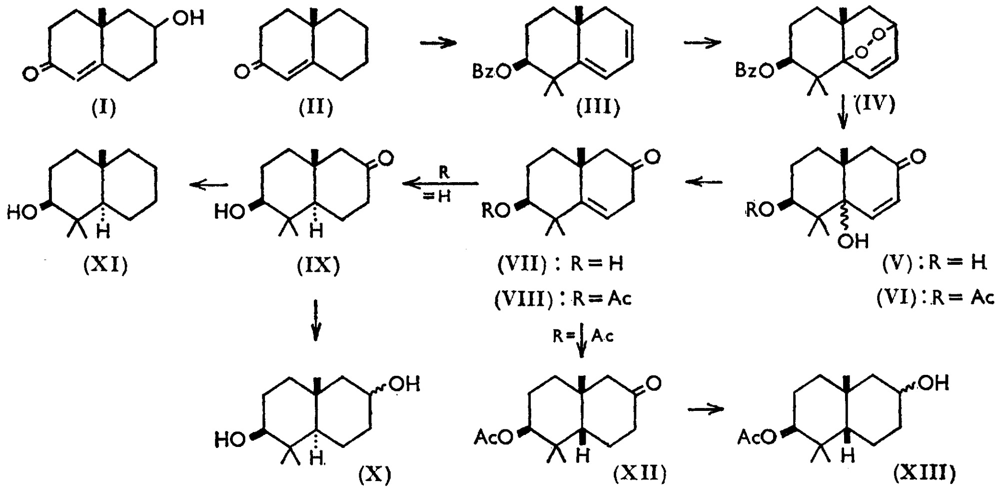
562. *Studies in the Synthesis of Terpenes. Part IV.* The Synthesis of* (±)-6β-*Hydroxy*-5 : 5 : 9β-*trimethyl*-trans-*decal*-2-*one.*

By T. G. Halsall, W. J. Rodewald, and (in part) D. Willis.

(±)-6β-Hydroxy-5 : 5 : 9β-trimethyl-*trans*-decal-2-one, a potential intermediate for the synthesis of higher terpenes, has been synthesised from 10-methyl-$\Delta^{1(9)}$-octal-2-one.

One of the potential intermediates for the synthesis of onocerin and of pentacyclic triterpenes of the β-amyrin type is the hydroxydecalone[1] (IX). A way of synthesising this appeared to be from derivatives of 4-hydroxy-2-methylcyclohexanone which, by analogy with 2-methylcyclohexanone, might be expected to condense with 4-diethylaminobutan-2-one to give the octalone (I). However, attempts to obtain this octalone from both the benzoate and the tetrahydropyranyl ether of 4-hydroxy-2-methylcyclohexanone were unsuccessful. The octalone has recently been prepared from the benzoate in about 2% yield by Sondheimer and Elad[2] but its further transformation to the decalone (IX) was not pursued.



The decalone (IX) has now been prepared in reasonable overall yield from the octalone (II).[3,4] This was converted into the diene (III) essentially by the method of King, Ritchie, and Timmons[5] (cf. the experimental section for brief details). The diene was then irradiated at room temperature in ethanol containing eosin (10% of the weight of diene) in

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* Part III, *J.*, 1958, 624.

[1] Halsall and Thomas, *J.*, 1958, 2431.

[2] Sondheimer and Elad, *J. Amer. Chem. Soc.*, 1957, **79**, 5544.

[3] Du Feu, McQuillin, and Robinson, *J.*, 1937, 53.

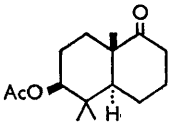
[4] Gaspert, Halsall, and Willis, *J.*, 1958, 624.

[5] King, Ritchie, and Timmons, *Chem. and Ind.*, 1956, 1230.

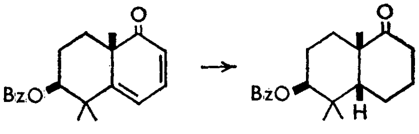
the presence of oxygen.[6] A product was obtained which at first appeared homogeneous but on crystallisation from ethanol gave two compounds as well as a small amount of oil. The main compound, obtained in 60% yield after recrystallisation, was the epidioxide (IV). Its structure, apart from the configuration of the epidioxide group, follows from the reactions subsequently carried out with it. The configuration is probably α, the 5- and 9-methyl groups preventing β-attack of oxygen. The other compound was isomeric with the epidioxide (IV).

When the epidioxide (IV) was treated with hot methanolic alkali, not only hydrolysis of the benzoate group but also rearrangement of the epidioxide group occurred. The product was the unsaturated ketone (V). In an attempt to cut down the losses involved in the crystallisation of the epidioxide (IV) the crude product from the irradiation was treated with alkali, it being expected that the resulting αβ-unsaturated ketone (V) would be readily separated from the simple hydrolysis product of the isomeric benzoate. The overall yield of ketone (V) obtained from the diene (III) by this procedure was much higher than that by the route involving crystallisation of the irradiation product. This suggested that the isomeric compound was produced after the irradiation and during the crystallisation of the epidioxide. This was proved by boiling the epidioxide in ethanol, the isomeric compound then being formed almost quantitatively. An analogous thermal rearrangement of an epidioxide is that of ascaridole to isoascaridole in hot xylene.[7] It is probable that the isomeric compound is analogous to isoascaridole. Its structure will be discussed in a later communication.

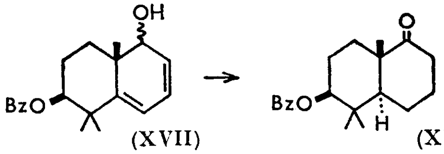
The alkaline rearrangement of the epidioxide (IV) to the ketone (V) is typical of secondary-tertiary epidoxides.[8,9] The light absorption of the ketone (V) ($\lambda_{max.}$ 2220 Å; ε 8950) and of its 6β-acetate (VI) shows the typical hypsochromic effect found with αβ-unsaturated γ-hydroxy-ketones.[8]



(XIV)



(XV) (XVI)



(XVII) (XVIII)

The γ-hydroxy-ketone (V) was reduced with zinc dust in boiling acetic acid[10] to the βγ-unsaturated ketone (VII); no evidence was found for the presence of the conjugated ketone. Hydrogenation of the ketone (VII) with palladium–charcoal in ethanol or acetic acid gave the *trans*-decalone (IX). Hydrogention with Adams platinum catalyst in acetic acid afforded the *trans*-decalindiol (X) which was similarily obtained from the *trans*-decalone. No *cis*-decalin derivative was found in the products of these hydrogenations.

Wolff–Kishner reduction of the *trans*-decalone gave the known *trans*-decalol (XI).[4]

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[6] Cf. Bergmann and McLean, *Chem. Rev.*, 1941, **28**, 367; Bladon, Clayton, Greenhalgh, Henbest, Jones, Lovell, Silverstone, Wood, and Woods, *J.*, 1952, 4883; Clayton, Henbest, and Jones, *J.*, 1953, 2015; Bladon, *J.*, 1955, 2176.

[7] Henry and Paget, *J.*, 1921, **119**, 1722; Simonsen, " The Terpenes," Cambridge Univ. Press, 2nd edn., Vol. I, p. 447.

[8] Cf. Conca and Bergmann, *J. Org. Chem.*, 1953, **18**, 1104.

[9] Cf. Laubach, Schreiber, Agnello, Lightfoot, and Brunings, *J. Amer. Chem. Soc.*, 1953, **75**, 1514; Kornblum and de la Mare, *ibid.*, 1951, **73**, 880.

[10] Cf. Rosenfeld and Gallagher, *ibid.*, 1955, **77**, 4367, and references cited therein.

This has also been obtained from the acetoxydecalone[4] (XIV) which has been shown by Sondheimer and Elad[11] to have the acetoxyl and the angular methyl group *cis*-related.

Acetylation of the unsaturated γ-hydroxy-ketone (V) gave the 6β-monoacetate (VI). Reduction of this with zinc dust in acetic acid gave the β-unsaturated acetoxy-ketone (VIII). Hydrogenation with palladium–charcoal then gave the acetoxydecalone (XII). This must be a *cis*-decalin derivative as it and the alcohol derived from it are different from the corresponding *trans*-decalone (IX) and its acetate. Hydrogenation with Adams platinum catalyst gave the acetoxy-*cis*-decalol (XIII), also obtained by hydrogenation of the corresponding ketone (XII). The unpredictability of the course of hydrogenation is further illustrated by the results of Haynes and Timmons[12] who have shown that hydrogenation of the dienone (XV) gives a *cis*-decalone (XVI), whilst hydrogenation of the dienol (XVII) followed by oxidation of the resulting alcohol afforded the *trans*-decalone (XVIII).

EXPERIMENTAL

M. p.s were determined on a Kofler block and are corrected. The light petroleum used for chromatography had b. p. 40—60°; that used for crystallisations had b. p. 60—80°. The alumina used for chromatography was " Peter Spence, Grade H," deactivated with 5% of 10% acetic acid.

(±)-2β-*Benzoyloxy*-1 : 2 : 3 : 4 : 5 : 10-*hexahydro*-1 : 1 : 10β-*trimethylnaphthalene*.—This was prepared by the following reactions essentially according to the method of Haynes, King, Ritchie, and Timmons.[5,13] 10-Methyl-$\Delta^{1(9)}$-octal-2-one was prepared from 2-methylcyclohexanone and 4-diethylaminobutan-2-one. It was methylated with methyl iodide in the presence of sodium t-amyloxide, to give 1 : 1 : 10-trimethyl-Δ^{8}-octal-2-one in 80% yield. This in turn was converted into 2β-benzoyloxy-1 : 1 : 10β-trimethyl-Δ^{8}-octalin, m. p. 87—89° (Haynes, King, Ritchie, and Timmons[13] give m. p. 87—89°), in 40—50% yield by reduction with sodium in boiling ethanol and benzoylation of the crude product.

The benzoate, with *N*-bromosuccinimide in boiling carbon tetrachloride, gave the 7-bromo-derivative, m. p. 153—155° (Haynes, King, Ritchie, and Timmons[13] give m. p. 153—155°), in 95% yield. This was dehydrobrominated by heating it in ethanol, (±)-2β-benzoyloxy-1 : 2 : 3 : 4 : 5 : 10-hexahydro-1 : 1 : 10β-trimethylnaphthalene, m. p. 103—105° (Haynes, King, Ritchie, and Timmons[13] give m. p. 101—104°), being obtained in 90% yield.

The last benzoate with aqueous-alcoholic potassium hydroxide gave (±)-2β-*hydroxy*-1 : 2 : 3 : 4 : 5 : 10-*hexahydro*-1 : 1 : 10β-*trimethylnaphthalene* as prisms (from light petroleum), m. p. 83—84° (Found: C, 80·9; H, 10·8. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%), $\lambda_{max.}$ 2650 Å (ε 3700). The hydroxy-compound (2·52 g.), with acetic anhydride (3 c.c.) and pyridine (10 c.c.) in the usual way, afforded an oil which was taken up in light petroleum and filtered through alumina (10 g.) along with light petroleum (100 c.c.). Evaporation of the solvent and distillation of the product gave (±)-2β-*acetoxy*-1 : 2 : 3 : 4 : 5 : 10-*hexahydro*-1 : 1 : 10β-*trimethylnaphthalene* (2·27 g.), b. p. 62°/0·03 mm., $n_D^{12·5}$ 1·5065 (Found: C, 77·0; H, 9·75. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·45), $\nu_{max.}$ 1740 (OAc), 1680 and 700 cm.$^{-1}$ (no band due to OH), $\lambda_{max.}$ 2640 Å (ε 3940).

(±)-2β-*Benzoyloxy*-6 : 9-*epidioxy*-1 : 1 : 10β-*trimethyl*-Δ^{7}-*octalin* (IV).—Dry oxygen was passed into (±)-2β-benzoyloxy-1 : 2 : 3 : 4 : 5 : 10-hexahydro-1 : 1 : 10β-trimethylnaphthalene (10 g.) in ethanol (300 c.c.) containing eosin (1·0 g.) and illuminated by a 500-watt lamp placed beneath the reaction flask which was kept at 17° by immersion in flowing water. After 6 hr. a solid began to separate. After 24 hr. irradiation was stopped, and the mixture kept at 0° overnight. The resulting solid (A) (7·0 g.), m. p. 162°, was removed. Evaporation of the solvent at a low temperature afforded a further quantity of solid (B) (3·15 g.), m. p. ~160°, and an oil (C) (1·0 g.). The solid (B) was extracted with benzene to separate it from eosin. The resulting benzene solution was evaporated, and the residue combined with solid (A) and crystallised several times from ethanol, to give two compounds: (i) (±)-2β-*benzoyloxy*-6 : 9-*epidioxy*-1 : 1 : 10β-*trimethyl*-Δ^{7}-*octalin* (6·6 g., 60%), elongated prisms, m. p. 168° (softening at 160°) (Found: C, 73·05; H, 7·5. $C_{20}H_{24}O_4$ requires C, 73·15; H, 7·35%), $\nu_{max.}$ 1728 (benzoate), 1380 and 1368 (*gem*-dimethyl)

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[11] Sondheimer and Elad, *J. Amer. Chem. Soc.*, 1958, **80**, 1967.

[12] Haynes and Timmons, *Proc. Chem. Soc.*, 1958, 345.

[13] Haynes, King, Ritchie, and Timmons, unpublished work.

and 888 cm.$^{-1}$ (epidioxide), and (ii) an isomeric *benzoate* (3·4 g., 31%), plates, m. p. 172° (softening at 165°) (Found: C, 72·85; H, 7·15. $C_{20}H_{24}O_4$ requires C, 73·15; H, 7·35%), $\nu_{max.}$ 1728 (benzoate), 1378 and 1362 (*gem*-dimethyl), and 910 and 828 cm.$^{-1}$ (epoxy-groups?).

(±)-6β : 10ξ-*Dihydroxy*-5 : 5 : 9β-*trimethyl*-Δ³-*octal*-2-*one* (V).—(*a*) The epidioxide benzoate (IV) (1·0 g.) was heated under reflux in aqueous-methanolic potassium hydroxide (10%; 25 c.c.) for 1 hr. After removal of the methanol under reduced pressure, dilution with water and extraction with chloroform afforded (±)-6β : 10ξ-*dihydroxy*-5 : 5 : 9β-*trimethyl*-Δ³-*octal*-2-*one* which crystallised from ethanol–light petroleum (1 : 25) as prisms (670 mg., 98%), m. p. 181° (Found: C, 69·65; H, 9·25. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%), $\lambda_{max.}$ 2220 Å (ε 8800), $\nu_{max.}$ 3460 (OH), 1680 (C=C–C=O), 1382 and 1368 cm.$^{-1}$ (*gem*-dimethyl). The *semicarbazone* was obtained as plates (from aqueous ethanol), m. p. 254—255° (decomp.) (Found: C, 59·95; H, 8·3; N, 15·15. $C_{14}H_{23}O_3N_3$ requires C, 59·75; H, 8·25; N, 14·95%).

(*b*) (±)-2β-Benzoyloxy-1 : 2 : 3 : 4 : 5 : 10-hexahydro-1 : 1 : 10β-trimethylnaphthalene (15 g.) was irradiated in ethanol (350 c.c.) containing eosin (1·5 g.) in the presence of oxygen as above. After 6 hr. a solid began to separate. After irradiation for 28 hr. the mixture was kept at 0° overnight; a solid (12·5 g., m. p. 162—165°) separated. It was isolated and washed with ethanol. Low-temperature evaporation of the solvent afforded a further quantity of solid (2 g.; m. p. 160—163°) and an oil (~2·0 g.).

The solids were combined and part (500 mg.) was adsorbed from benzene (15 c.c.) on alumina (30 g.). Elution with benzene–light petroleum (1 : 1) afforded (±)-2β-benzoyloxy-6 : 9-epidioxy-1 : 1 : 10β-trimethyl-Δ⁷-octalin (490 mg.) as prisms, m. p. 168° [after one recrystallisation from benzene–light petroleum (2 : 1)].

The combined solids (10 g.) were heated under reflux with aqueous-methanolic potassium hydroxide (10%; 200 c.c.) for 3 hr. After removal of the solvent under reduced pressure and dilution with water, extraction with chloroform afforded (±)-6β : 10ξ-dihydroxy-5 : 5 : 9β-trimethyl-Δ³-octal-2-one as needles (6·30 g.) [from ethanol–light petroleum (1 : 25)], m. p. 181°.

Rearrangement of (±)-2β-*Benzoyloxy*-6 : 9-*epidioxy*-1 : 1 : 10β-*trimethyl*-Δ⁷-*octalin in Boiling Ethanol.*—The epidioxide benzoate (500 mg.) was heated under reflux in ethanol (50 ml.) for 5 hr. The solution was then concentrated and the product, m. p. 169—170°, was recrystallised twice from ethanol to give the isomeric benzoate described above as plates (450 mg.), m. p. 172°.

(±)-6β-*Hydroxy*-5 : 5 : 9β-*trimethyl*-Δ⁴-*octal*-2-*one* (VII).—6β : 10-Dihydroxy-5 : 5 : 9β-trimethyl-Δ³-octal-2-one (1·8 g.) in boiling acetic acid (40 c.c.) was treated during 15 min. with small portions of zinc dust (2·2 g.). The mixture was heated under reflux for a further 5 min. and then filtered, the residue being washed with chloroform. After addition of further chloroform to the filtrate, the acetic acid was removed by washing with aqueous sodium hydrogen carbonate. A viscous oil was isolated from the chloroform solution. It was adsorbed from benzene–light petroleum (1 : 3) on deactivated alumina (150 mg.). Elution with the same solvent mixture gave (±)-6β-*hydroxy*-5 : 5 : 9β-*trimethyl*-Δ⁴-*octal*-2-*one* which crystallised from ether–light petroleum (1 : 6) as prisms (1·2 g., 72%), m. p. 99° (Found: C, 74·8; H, 9·75. $C_{13}H_{20}O_2$ requires C, 74·95; H, 9·7%), $\lambda_{max.}$ 2800 Å (ε 39), $\nu_{max.}$ 3450 (OH), 1715 (sat. C=O), 1375 and 1360 (*gem*-dimethyl), 812 and 793 cm.$^{-1}$ (trisubstituted double bond). The octalone was not very stable. If it was kept dissolved in ethanol, ether, acetone, or light petroleum for some time, much oil was obtained on evaporation. The dry crystals began to soften after several weeks.

Elution with ether gave a light yellow oil (300 mg.), which crystallised from ether to give prisms (30 mg.), m. p. 264°. From the mother-liquor a further solid (20 mg.) was obtained after recrystallisation from ethanol–light petroleum. Further crystallisation from ethanol gave yellow prisms, m. p. 228—230°.

Hydrogenation of (±)-6β-*Hydroxy*-5 : 5 : 9β-*trimethyl*-Δ⁴-*octal*-2-*one* (VII).—(*a*) The octalone (400 mg.) was hydrogenated in ethanol (40 c.c.) with previously hydrogenated 10% palladium–charcoal (400 mg.). Hydrogenation was stopped after 50 min. when 1·03 mol. had been taken up. Removal of the catalyst and evaporation of the solvent gave (±)-6β-*hydroxy*-5 : 5 : 9β-*trimethyl*-trans-*decal*-2-*one* (IX) as prisms (380 mg., 94%) (from ether), m. p. 144—145° (sublimation at 115°) (Found: C, 74·0; H, 10·6. $C_{13}H_{22}O_2$ requires C, 74·25; H, 10·55%), $\nu_{max.}$ (in "Nujol") 3450 (OH), 1700 (C=O), 1382 and 1360 cm.$^{-1}$ (*gem*-dimethyl) (no band at 812 or 793 cm.$^{-1}$).

(*b*) The octalone (200 mg.) was hydrogenated in acetic acid (30 c.c.) with previously hydrogenated 10% palladium–charcoal (200 mg.). After 75 min. 1·0 mol. had been absorbed and hydrogenation was stopped. After removal of the catalyst and solvent, crystallisation from ether gave (±)-6β-hydroxy-5 : 5 : 9β-trimethyl-*trans*-decal-2-one (165 mg.), m. p. and mixed m. p. 144—145°.

(*c*) An attempt to hydrogenate the octalone (200 mg.) in ethyl acetate (20 c.c.) with Adams platinum catalyst (100 mg.) failed. Acetic acid (2 c.c.) was added and a slow uptake of hydrogen then took place. The reaction was stopped after 1 mol. had been absorbed. Removal of the catalyst and solvent gave a viscous oil, which was dissolved in ether and treated with light petroleum. The resultant precipitate (130 mg.) was crystallised several times from ether–light petroleum (1 : 10), to give 6β-hydroxy-5 : 5 : 9β-trimethyl-*trans*-decal-2-one (80 mg.), m. p. 144—145°, and 2ξ : 6β-dihydroxy-5 : 5 : 9β-trimethyl-*trans*-decalin (see next paragraph) (50 mg.), m. p. 190°.

(*d*) The octalone (200 mg.) in acetic acid (20 c.c.) was hydrogenated with Adams platinum catalyst (50 mg.). Uptake (2·05 mol.) ceased after 45 min. Removal of the catalyst and solvent afforded a solid which, crystallised from ether–light petroleum (1 : 5), gave 2ξ : 6β-*dihydroxy*-5 : 5 : 9β-*trimethyl*-trans-*decalin* (X) as prisms (180 mg.), m. p. 190° (Found: C, 73·4; H, 11·25. $C_{13}H_{24}O_2$ requires C, 73·55; H, 11·4%), $\nu_{max.}$ (in " Nujol ") 3350 cm.$^{-1}$ (OH) (no band indicative of C=O or trisubstituted double bond).

(*e*) The octalone (200 mg.) in ethanol (15 c.c.) was hydrogenated with Adams platinum catalyst (50 mg.). Absorption of hydrogen (0·8 mol.) was very slow and ceased after 4 hr. Removal of the catalyst and solvent gave a viscous oil which was adsorbed on deactivated alumina (20 g.). Elution with light petroleum–benzene (1 : 4) afforded starting material (120 mg., 60%). Elution with benzene gave an oil (35 mg.) which was not investigated further. Elution with ether yielded a solid (40 mg.) which crystallised from ether–light petroleum (1 : 3) to give 2ξ : 6β-dihydroxy-5 : 5 : 9β-trimethyl-*trans*-decalin (20 mg.), m. p. 190°, and a compound (15 mg.) (prisms), m. p. 211° (partial sublimation 205°) (Found: C, 68·35; H, 10·5%), $\nu_{max.}$ (in " Nujol ") at 3300 (OH) and 812 cm.$^{-1}$ (double bond) (no C=O band).

Hydrogenation of 6β-*Hydroxy*-5 : 5 : 9β-*trimethyl*-trans-*decal*-2-*one*.—The decalone (200 mg.) in acetic acid (20 c.c.) was hydrogenated with Adams platinum catalyst (50 mg.). Reaction was stopped after 20 min. when 1 mol. had been absorbed. Removal of the catalyst and solvent gave 2ξ : 6β-dihydroxy-5 : 5 : 9β-trimethyl-*trans*-decalin (195 mg.) (prisms from ether–light petroleum), m. p. and mixed m. p. 190°.

6β-*Acetoxy*-5 : 5 : 9β-*trimethyl*-trans-*decal*-2-*one*.—6β-Hydroxy-5 : 5 : 9β-trimethyl-*trans*-decal-2-one (60 mg.) in pyridine (1·5 c.c.) with acetic anhydride (0·15 c.c.) at 100° for 30 min. gave a product which crystallised from ether–light petroleum (1 : 6) to give 6β-*acetoxy*-5 : 5 : 9β-*trimethyl*-trans-*decal*-2-*one* as prisms (~70 mg.), m. p. 113°, depressed to 105—110° on admixture with the corresponding *cis*-decalone (see below) (Found: C, 71·45; H, 9·25. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·6%).

Wolff–Kishner Reduction of (±)-6β-*Hydroxy*-5 : 5 : 9β-*trimethyl*-trans-*decal*-2-*one* (IX).—The hydroxydecalone (700 mg.) in redistilled diethylene glycol (15 c.c.) was heated under reflux for 1 hr. under nitrogen with 100% hydrazine hydrate (1·4 c.c.) and potassium hydroxide (1·3 g.). The excess of water was then removed by distillation until the internal temperature reached 180°. Heating under reflux was then continued for a further 3 hr. under nitrogen. After dilution with water, ether-extraction afforded a solid (380 mg.) which on sublimation at 110—115°/12 mm. gave (±)-1 : 1 : 10β-trimethyl-*trans*-decalin-2β-ol (XI) as plates, m. p. and mixed m. p. 60—65° (Found: C, 79·85; H, 12·05. Calc. for $C_{13}H_{24}O$: C, 79·5; H, 12·3%), $\nu_{max.}$ (in " Nujol ") 3300 (OH) (no C=O band). The infrared spectrum was identical with that of authentic (±)-1 : 1 : 10β-trimethyl-*trans*-decalin-2β-ol.[4]

(±)-6β-*Acetoxy*-10ξ-*hydroxy*-5 : 5 : 9β-*trimethyl*-Δ^3-*octal*-2-*one* (VI).—6β : 10ξ-Dihydroxy-5 : 5 : 9β-trimethyl-Δ^3-octal-2-one (790 mg.) in pyridine (5 c.c.) with acetic anhydride (0·4 c.c.) at 100° for 1 hr. gave a product, m. p. 105—108°. Crystallisation from ethanol–light petroleum (1 : 20) gave (±)-6β-*acetoxy*-10ξ-*hydroxy*-5 : 5 : 9β-*trimethyl*-Δ^3-*octal*-2-*one* as plates (910 mg., 97%), m. p. 110°, resolidifying partially as prisms, m. p. 127° (Found: C, 67·3; H, 8·2. $C_{15}H_{22}O_4$ requires C, 67·65; H, 8·35%), $\lambda_{max.}$ 2220 Å (ε 8950), $\nu_{max.}$ 3620 and 3500 (OH), 1740 and 1240 (OAc), 1685 cm.$^{-1}$ (C=C–C=O).

Zinc Reduction of (±)-6β-*Acetoxy*-10ξ-*hydroxy*-5 : 5 : 9β-*trimethyl*-Δ^3-*octal*-2-*one*.—Zinc dust (1·8 g.) was added in small portions during 15 min. to a boiling solution of the octalone (1·7 g.) in acetic acid. The hot solution was filtered, the residue being washed with chloroform. The product was isolated as a viscous oil with chloroform, acetic acid being removed by washing with aqueous sodium hydrogen carbonate solution. The oil was absorbed from benzene (15 c.c.) on deactivated alumina (150 g.). Elution with light petroleum–benzene (2 : 3) (800 c.c.) gave (±)-6β-*acetoxy*-5 : 5 : 9β-*trimethyl*-$\Delta^{4(10)}$-*octal*-2-*one* (VIII) (1·2 g., 75%), m. p. 64—66°, which crystallised from ether as plates, m. p. 67° (Found: C, 72·05; H, 8·8. $C_{15}H_{22}O_3$ requires C, 71·95; H, 8·85%), $\lambda_{max.}$ 2850 Å (ε 38), ε_{2100} 1100, ε_{2150} 715, ε_{2200} 540, $\nu_{max.}$ 1738 and 1238 (OAc), shoulders at 1722 and 1708 cm.$^{-1}$, $\nu_{max.}$ (in " Nujol ") 1695 cm.$^{-1}$ (C=O).

The acetoxyoctalone is not very stable. After several hours' in solution in organic solvents a viscous oil (polymer?) results. The crystals soften after several weeks.

Elution with light petroleum–benzene (2 : 3) (600 c.c.) gave a liquid fraction (100 mg.); addition of ether afforded a solid which crystallised from ethanol as light yellow prisms (substance A) (40 mg.), m. p. 266—267°, partial sublimation at 230° (Found: C, 73·1; H, 8·7%), $\lambda_{max.}$ (in chloroform) 2500 and 3550 Å ($E^{1\%}_{1\,cm.}$ 304, 410), $\nu_{max.}$ (in " Nujol ") 1732 and 1240 (OAc), 1695 (C=O), 1610 and 1580 cm.$^{-1}$ (no OH band).

Further elution with benzene (600 c.c.) and ether (400 c.c.) gave two liquid fractions (80 and 150 mg.). Several crystallisations of both fractions from alcohol or alcohol–light petroleum (1 : 4) afforded light yellow needles (*substance B*) (~100 mg.), m. p. 212—214°, resolidifying partially as yellow prisms, m. p. 253—254° (Found: C, 71·8; H, 7·75%; *M*, 408), $\lambda_{max.}$ (in chloroform) 2550 and 3550 Å ($E^{1\%}_{1\,cm.}$ 290, 457), $\nu_{max.}$ (in " Nujol ") 1730 and 1247 (OAc), 1710, 1685, 1590, 1575, 810, and 865 cm.$^{-1}$.

Substances A and B are probably acetates of the corresponding compounds, m. p. 264° and 228—230°, obtained as by-products from the reduction of 6β : 10ξ-dihydroxy-5 : 5 : 9β-trimethyl-Δ^3-octal-2-one with zinc.

Hydrogenation of (±)-6β-*Acetoxy*-5 : 5 : 9β-*trimethyl*-$\Delta^{4(10)}$-*octal*-2-*one*.—(*a*) The octalone (400 mg.) was hydrogenated in ethanol (40 c.c.) with previously hydrogenated 10% palladium–charcoal (400 mg.). After 30 min. 1·05 mol. had been absorbed and reaction was stopped. Removal of the catalyst and solvent gave a liquid which was dissolved in ether. Addition of light petroleum (4 vols.) gave (±)-6β-*acetoxy*-5 : 5 : 9β-*trimethyl*-cis-*decal*-2-*one* (XII) as prisms (220 mg., 54%), m. p. 108°, raised by further crystallisation from ether–light petroleum to 111°, depressed to 105—110° on admixture with the corresponding *trans*-decalone, m. p. 113° (Found: C, 71·3; H, 9·5. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·6%), $\nu_{max.}$ 1735 and 1240 (OAc), shoulder at 1725 cm.$^{-1}$ (C=O) (no band indicative of trisubstituted double bond). The spectrum was similar to that of (±)-6β-acetoxy-5 : 5 : 9β-trimethyl-*trans*-decal-2-one but differences were found at 1325, 1144, and 777 cm.$^{-1}$.

The acetate (100 mg.) was hydrolysed under reflux for 30 min. in 10% aqueous-methanolic potassium hydroxide (5 c.c.). The resulting (±)-6β-*hydroxy*-5 : 5 : 9β-*trimethyl*-cis-*decal*-2-*one* crystallised from ether–light petroleum as prisms (75 mg.), m. p. 111°, depressed to 106—111° on admixture with (±)-6β-hydroxy-5 : 5 : 9β-trimethyl-*trans*-decal-2-one (m. p. 144—145°) (Found: C, 74·35; H, 10·2. $C_{13}H_{22}O_2$ requires C, 74·25; H, 10·55%), $\nu_{max.}$ (in " Nujol ") 3400 (OH), 1702 cm.$^{-1}$ (C=O) (no band due to OAc). The spectrum was very similar to that of 6β-hydroxy-5 : 5 : 9β-trimethyl-*trans*-decal-2-one, but there was a small difference at 1133 cm.$^{-1}$.

(*b*) The octalone (200 mg.) was hydrogenated in acetic acid (15 c.c.) with Adams platinum catalyst (100 mg.). Uptake ceased after 85 min. (2 mol.). Removal of the catalyst and solvent afforded (±)-6β-*acetoxy*-5 : 5 : 9β-*trimethyl*-cis-*decalin*-2ξ-*ol* which crystallised from ether–light petroleum (1 : 4) as prisms (90 mg., 44%), m. p. 124° (Found: C, 71·0; H, 10·5. $C_{15}H_{26}O_3$ requires C, 70·8; H, 10·3%), $\nu_{max.}$ 3610 (OH), 1736 and 1240 cm.$^{-1}$ (OAc) (no band for C=O or trisubstituted double bond).

The acetate (50 mg.) was hydrolysed under reflux for 20 min. in 10% aqueous-methanolic potassium hydroxide (4 c.c.). The resulting (±)-5 : 5 : 9β-*trimethyl*-cis-*decalin*-2ξ : 6β-*diol* crystallised from ethanol–light petroleum as prisms (40 mg.), m. p. 158° (Found: C, 73·45; H, 11·4. $C_{13}H_{24}O_2$ requires C, 73·55; H, 11·4%), $\nu_{max.}$ (in " Nujol ") 3450 cm.$^{-1}$ (OH) (no band for OAc, C=O, or trisubstituted double bond).

Hydrogenation of (±)-6β-*Acetoxy*-5 : 5 : 9β-*trimethyl*-cis-*decal*-2-*one*.—The acetoxy-decalone (200 mg.) was hydrogenated in acetic acid (15 c.c.) in the presence of Adams platinum catalyst (50 mg.). The hydrogenation (1 mol.) was stopped after 1·5 hr. Removal of the catalyst and solvent gave an oil which gave crystals, m. p. 110—120°, from ether (0·5 ml.). The crystals were recrystallised from ether–light petroleum (1 : 4) to give (±)-6β-acetoxy-5 : 5 : 9β-trimethyl-*cis*-decalin-2ξ-ol as prisms (25 mg.), m. p. and mixed m. p. 124°.

Hydrogenation of (±)-6β : 10ξ-*Dihydroxy*-5 : 5 : 9β-*trimethyl*-Δ^3-*octal*-2-*one*.—The octalone

(500 mg.) in ethanol (30 c.c.) was hydrogenated with Adams platinum catalyst (80 mg.); 1·03 mol. was absorbed in 20 min. after which hydrogenation was stopped. Removal of the catalyst and solvent gave crude (±)-6β : 10ξ-*dihydroxy*-5 : 5 : 9β-*trimethyldecal*-2-*one* (500 mg.), m. p. 165°. Several crystallisations from ethanol–light petroleum (b. p. 60—80°) (1 : 20) afforded two types of crystal: needles, m. p. 170° (Found: C, 68·95; H, 9·9. $C_{13}H_{22}O_3$ requires C, 69·0; H, 9·6%), and prisms, m. p. 199° (Found: C, 69·0; H, 9·6%). These two forms were polymorphs since slow crystallisation of the former from ethanol–light petroleum (b. p. 60—80°) (1 : 5) gave the latter, and quick recrystallisation of the latter from light petroleum (b. p. 60—80°)–ether (20 : 1) afforded the former. Both forms had $\lambda_{max.}$ 2850 Å (ε 16), $\nu_{max.}$ (in "Nujol") 3410 (OH) and 1695 (sat. C=O) (no band due to ‒C=C‒C=O or double bond). They gave the same *acetate*: *e.g.*, the form, m. p. 170° (350 mg.), in pyridine (3 c.c.) with acetic anhydride (0·2 c.c.) at 100° for 30 min. gave prisms [from light petroleum (b. p. 60—80°)–ethanol (10 : 1)], m. p. 138° (Found: C, 67·3; H, 9·15. $C_{15}H_{24}O_4$ requires C, 67·15; H, 9·0%).

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