535. *The Reduction of 9-Methyl-*$\Delta^{5(10)}$*-octalin-*1,6*-dione.*

By C. B. C. Boyce and J. S. Whitehurst.

A high degree of stereospecificity is observed in the reduction of the diketone (I) named in the title and of some of its derivatives, either a *cis*- or a *trans*-ring junction being established readily. The constitution of the epimeric alcohols resulting from reduction of the diketone by lithium aluminium hydride has been determined. Two non-stereospecific reactions are the catalytic reduction of the derived hydroxy-ketone (II) and of its enol acetate.

9-METHYL-$\Delta^{5(10)}$-OCTALIN-1,6-DIONE (I) is a potential steroid and terpene intermediate. Several researches [1] using it were published during the course of our work, and in this paper some other aspects of its chemistry are recorded, more particularly its reduction.

At the outset two reference compounds were required, namely, the saturated diketones with *cis*- and *trans*-ring junctions. Nazarov *et al.*[2] prepared the former by catalytic reduction of compound (I) and proved the *cis*-ring junction by isolating the same compound from a Diels–Alder reaction; we have confirmed Nazarov's work. Despite a recent report [3] that lithium–ammonia reduction of the diketone (I) gave a complicated mixture we found that when ammonia distilled from sodium is used this reduction gives, in good yield, a ketone isomeric with that above; this was therefore the *trans*-compound.

Cocker and Halsall [1] first reported stereospecific reduction of diketone (I) by sodium borohydride to the hydroxy-ketone (II), where the hydroxyl group is *cis* to the methyl group, and stated that alkali-free sodium borohydride (crystallised from isopropylamine) was necessary. Strict adherence to these conditions furnished the hydroxy-ketone (II) as

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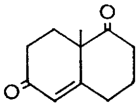
[1] Cocker and Halsall, *J.*, 1957, **3441**; *Chem. and Ind.*, 1956, 1275; Elad and Sondheimer, *Bull. Res. Council Israel*, 1956, **5**, *A*, 267; *Proc. Chem. Soc.*, 1957, 206; 1957, 320; *J. Amer. Chem. Soc.*, 1957, **79**, 5542; Halsall, Rodewald, and Willis, *Proc. Chem. Soc.*, 1958, 231; King, Ritchie, and Timmons, *Chem. and Ind.*, 1956, 1230; Haynes and Timmons, *Proc. Chem. Soc.*, 1958, 345; Swaminanthan and Newman, *Tetrahedron*, 1958, **2**, 88.

[2] Nazarov, Zav'yalov, Burmistrova, Gurvich, and Shmonina, *Zhur. obshchei Khim.*, 1956, **26**, 1441; *Chem. Abs.*, 1956, **50**, 13,847.

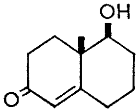
[3] Prelog and Zäch, *Helv. Chim. Acta*, 1959, **42**, 1862.

well as 16% of an unsaturated diol (III). Whilst we agree with Halsall that the use of sodium borohydride recrystallised from isopropylamine (or, preferably, from ethylene glycol dimethyl ether [4]) improved the quality of the product, it was found equally important to use the exact equivalent of borohydride, the compound (II) then being obtained in up to 92% yield. In agreement with Prelog *et al.*,[5] who used an optically active form of the hydroxy-ketone (II), we found the catalytic reduction of this compound to be non-stereospecific.

The hydroxy-ketone readily gave an acetate which on hydrogenation in ethanol over palladium–strontium carbonate furnished a single product. Hydrolysis gave a saturated hydroxy-ketone, m. p. 67—68°. As this evidently differed from a compound, m. p. 91°, prepared by Jaeger,[6] for which a *cis*-ring junction had been claimed, it was considered to be the *trans*-compound. This view was apparently strengthened when lithium–ammonia reduced the hydroxy-ketone (II) to a compound, also of m. p. 67—68°.[7] However, whereas the lithium–ammonia product gave the expected *trans*-diketone on oxidation, the product obtained by hydrogenating the acetate yielded the *cis*-diketone and therefore has structure (IV). Mixed melting point and infrared comparisons of the two hydroxy-ketones showed that they were indeed different. This left only the discrepancy between the melting point claimed by Jaeger (91°) and by ourselves (67—68°) for the *cis*-ketol (IV). Jaeger's product had been obtained by hydrogenation and hydrolysis of the tetrahydropyranyl ether of a hydroxy-ketone (presumably II) which itself was prepared by the reduction of the enol ether of the diketone (I) by lithium aluminium hydride. We made the tetrahydropyranyl ether of the hydroxy-ketone (II), the latter having been made by reduction of the diketone with sodium borohydride. Our ether, on hydrogenation and hydrolysis, gave a product, m. p. 67—68°, which was identical with that obtained by the acetate route. A specimen, kindly provided by Dr. Jaeger, was not, however, identical with ours. As the only difference in the two preparations involves a different route to the starting ketol (II), it is possible that Jaeger's initial ketol could have been the 1-epimer of (II).



(I)



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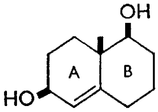

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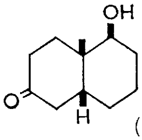

(IV)

Reduction of the diketone (I) by lithium aluminium hydride gave two compounds, the major component being identical with that obtained by use of sodium borohydride. The two products were 6-epimers of the hydroxy-ketone (III) since manganese dioxide oxidised each to the same hydroxy-ketone (II).

Structures were assigned to these compounds by the following considerations. Models reveal that, provided boat forms are not involved, the presence of a secondary-tertiary double bond in an octalin derivative such as (III) imposes a unique conformation on the ring to which it is exocyclic [partial structure (IIIA)]. Ring B cannot change to the alternative chair form (IIIB) because the 8,9 bond would then become axial and it would be impossible to form ring A [it is noteworthy that structure (IIIC) is enantiomeric with, and configurationally different from, (IIIA)]. Ring B of the diol (III) is thus analogous to the steroid ring B. Now reduction [8] of cholest-4-en-3-one by lithium aluminium hydride yields 70% of the 3β-alcohol and 24% of the 3α-epimer. By analogy the compound melting at 145—146° should be the 3β-alcohol (III) (the 9-methyl group being arbitrarily labelled β).

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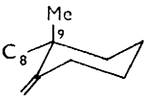
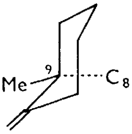
[4] Brown, Mead, and Subba Rao, *J. Amer. Chem. Soc.*, 1955, **77**, 6209.
[5] Prelog, Acklin, and Zäch, *Helv. Chim. Acta*, 1958, **41**, 1428.
[6] Jaeger, *Tetrahedron*, 1958, **2**, 326.
[7] This compound has been obtained by the same method by Birch, Pride, and Smith (*J.*, 1958, 4688).
[8] Dauben, Micheli, and Eastham, *J. Amer. Chem. Soc.*, 1952, **74**, 3852.

A more detailed examination of the model of the diol (III) shows that by C–C rotation at positions 6, 7, and 8 the two half-chair conformations[9] of ring A are obtained. The conformation (IIID) has a *quasi*-equatorial hydroxyl group, the other (IIIE) a *quasi*-axial hydroxyl group. For the $C_{(6)}$-epimer of (III) (the 1β,6α-diol) this relation is reversed. Conformation (IIID) is energetically favoured over (IIIE), but for the 6-epimer the relation is not so certain. We hoped that infrared-absorption studies would furnish some information on this matter but, as will be reported later, the spectra of these bicyclic alcohols proved to be considerably more complex than those of their steroid analogues.[10] However, one observation supporting structure (III) (and IIID) for the compound of m. p. 145—146° was that with acetic anhydride and pyridine it gave a diacetate whereas the epimer of m. p. 140° more readily underwent dehydration, thus demonstrating a greater axial character for its allylic hydroxyl group.



(IIIA)



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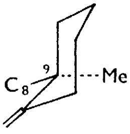
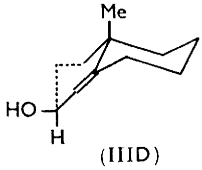


(IIIC)



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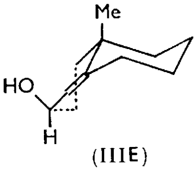


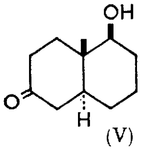
(IIIE)

The following chemical evidence was decisive. Catalytic reduction of the enediol, m. p. 145—146°, under defined conditions gave as one product a saturated diol, m. p. 133°, which was readily converted on oxidation into the *trans*-diketone. The same saturated diol was also obtained by reduction of either the *trans*-hydroxy-ketone (V) or the enedione (I) by lithium, ammonia, and ethanol. As the *trans*-structure is unique it follows that the 6-hydroxyl group formed will be equatorial (β). The enediol, m. p. 145—146°, thus has structure (III).

The other hydrogenation product from the diol (III), and the only one when the reaction was not interrupted, was 9-methyl-*trans*-1β-decalol, hydrogenolysis of the allylic hydroxyl group having occurred. The compound was characterised as the 3,5-dinitrobenzoate and on oxidation gave the known 9-methyl-*trans*-decal-1-one,[11] from which a semicarbazone and a dinitrophenylhydrazone, identical with specimens kindly provided by Professor W. S. Johnson (Wisconsin), were secured.

Mild acid-dehydration of the mixed allylic alcohols (III and its epimer) gave a homogeneous product formulated as (VI) in which the distribution of double bonds was inferred from its ultraviolet absorption maximum at 235 mμ (ε 17,300). Chromic acid oxidation produced the corresponding ketone without extension of the conjugation. The dienol on catalytic reduction gave stereospecifically *trans*-9-methyl-1β-decalol.

It was of interest to compare the behaviour of other 3,5-diene systems. The enol ether (VII) was readily made from the diketone (I) and ethyl orthorformate in benzene–ethanol containing a trace of hydrochloric acid. Under more vigorous conditions (cf. Swaminanthan *et al.*[1]) the high yield of product indicated further attack by the reagent, probably at the 1-carbonyl group. Catalytic reduction of the ether (VII) in ethanol over palladium–strontium carbonate stopped after absorption of 1 mol. of hydrogen and the product (formulated as VIII) afforded, on hydrolysis, a good yield of the pure *trans*-diketone.



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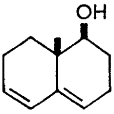

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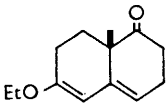

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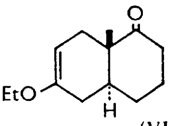

(VIII)

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[9] Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21.

[10] Cf. Dauben and Hoerger, *J. Amer. Chem. Soc.*, 1951, **73**, 1504; Dauben and Freeman, *ibid.*, 1952, **74**, 5206; Baker, Minckler, and Hussey, *ibid.*, 1959, **81**, 2379.

[11] Johnson, *J. Amer. Chem. Soc.*, 1943, **65**, 1317.

The reduction of an enol acetate was next investigated. To avoid complications with the 1-carbonyl group an enol acetate was prepared from the hydroxy-ketone (II). Its light absorption was consistent with a 3,5-diene structure. In the presence of Adams catalyst in ethanol it rapidly absorbed three mols. of hydrogen. Removal of the 1-acetyl group from the product by lithium aluminium hydride, and oxidation, gave an oil which was shown by the formation of derivatives to be a mixture of 9-methyl-*cis*- and -*trans*-1-decalone. Hydrogenolysis at the 6-position was not unexpected as a similar case has been reported for a steroid,[12] where, however, only the *trans*-ring junction resulted.

EXPERIMENTAL

All compounds are racemic; the angular methyl group (designated β in the one enantiomer named) is chosen as reference point. Ultraviolet light absorption data refer to EtOH solutions.

*9-Methyl-*cis*-decalin-1,6-dione.*—A solution of 9-methyl-$\Delta^{5(10)}$-octalin-1,6-dione (3·0 g.) in ethanol (25 ml.) was added to a pre-hydrogenated suspension of platinum oxide (100 mg.) in ethanol (25 ml.) and shaken at room temperature and pressure with hydrogen. Uptake ceased after 10 min. The catalyst was removed and the solvent was evaporated under reduced pressure. Chromatography of the residue on alumina gave a solid fraction which crystallised from light petroleum–ether to afford the *cis*-dione (2·4 g.), m. p. 65° (lit.,[2] m. p. 61—63°) (Found: C, 73·4; H, 8·6. Calc. for $C_{11}H_{16}O_2$: C, 73·3; H, 9·0%), $\nu_{max.}$ (in Nujol) 3000, 1702, 1178, 1144, 1020, 1002, and 912 $cm.^{-1}$.

The bis-2,4-dinitrophenylhydrazone was an orange powder (from tetrahydrofuran), m. p. 230·5—231·5° (lit.,[2] m. p. 230·5—231·5°) (Found: C, 50·9; H, 4·5; N, 20·1. Calc. for $C_{23}H_{24}O_8N_8$: C, 51·1; H, 4·5; N, 20·7%).

*9-Methyl-*trans*-decalin-1,6-dione.*—A solution of the dione (I) (3·0 g.) in tetrahydrofuran (50 ml.) was added dropwise during 30 min. to a stirred solution of lithium (300 mg.) in redistilled liquid ammonia (200 ml.). After 15 min. ammonium chloride was added to discharge the blue colour. The ammonia was evaporated and the residue extracted with ether. The oil (3·08 g.) left after removal of solvent slowly crystallised and was converted into a *bis-2,4-dinitrophenylhydrazone* which was shown to be homogeneous by paper chromatography and chromatography on 4 : 1 bentonite–kieselguhr. It had m. p. 231° (from chloroform–ethanol) (depression on admixture with the *cis*-derivative) (Found: C, 51·0; H, 4·3; N, 21·0%).

5β-Hydroxy-10β-methyl-$\Delta^{1(9)}$*-2-octalone* (II).—This was best prepared as follows: sodium borohydride (850 mg.) in ethanol (200 ml.) (some solid remained undissolved) was added dropwise during 1 hr. to a stirred solution of the dione (13·55 g.) in ethanol (100 ml.) at 0°. After a further 15 min. acetic acid was added. All solvent was removed at reduced pressure and the residue was dissolved in chloroform and treated with water. The organic layer was dried ($MgSO_4$) and distilled to give the anhydrous hydroxy-ketone, b. p. 140°/0·25 mm. (12·75 g., 92%) (Jaeger[6] gives b. p. 135—137°/0·2 mm.). The oil solidified on exposure to air and crystallised from moist ether as the monohydrate, m. p. 58—59°. The infrared spectrum (liquid film) had main bands at 3500, 3000, 1662 (C:C·C=O), 1140, 1086, 1035, 1007, 960, and 870 $cm.^{-1}$.

5β-Acetoxy-10β-methyl-$\Delta^{1(9)}$*-2-octalone.*—Anhydrous 5β-hydroxy-10β-methyl-$\Delta^{1(9)}$-2-octalone (11·4 g.) was treated with acetic anhydride (35 ml.) and pyridine (50 ml.) and left overnight at room temperature. Crystallisation from light petroleum gave the *acetate* (11·3 g., 80%), m. p. 89° (Found: C, 70·3; H, 8·5. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%), $\nu_{max.}$ (in Nujol) 1734 (ester), 1670 (C:C·C=O), 1258, 1238, 1218, 1032, 1010, 990, 936, and 880 $cm.^{-1}$.

*5β-Acetoxy-10β-methyl-*cis*-2-decalone.*—The foregoing acetate (4·49 g.) in ethanol (50 ml.) was hydrogenated over 2% palladium–strontium carbonate (2·0 g.). Uptake of hydrogen ceased at 1 mol. after 15 min. Removal of catalyst and solvent gave an oil which crystallised from isopentane at −20° to give the *decalone* (4·1 g.), m. p. 50·5—51° (Found: C, 69·8; H, 8·8. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%), $\nu_{max.}$ (in Nujol) 1724 (ester), 1706 (C=O), 1240 (acetate, simple), 1170, 1056, 1020, 976, and 960 $cm.^{-1}$.

*5β-Hydroxy-10β-methyl-*cis*-2-decalone.*—A solution of the acetoxy-*cis*-decalone (4·0 g.) in ethanol (25 ml.) was refluxed with potassium hydroxide (1 g.) for 90 min. Working up in the usual way gave the cis-*hydroxy-ketone* (2·35 g., 72%) which crystallised as thick flat prisms,

[12] Inhoffen, G. Stoeck, Kölling, and V. Stoeck, *Annalen*, 1950, **568**, 52.

m. p. 67—68° from light petroleum containing a few drops of ether (Found: C, 71·7; H, 9·8. $C_{11}H_{18}O_2$ requires C, 71·5; H, 10·0%), $\nu_{max.}$ (liquid film) 3500, 1706, 1448, 1420, 1170, 1120, 1056, 1032, 1000, 960, and 790 cm.$^{-1}$. Its mixture with 5β-hydroxy-10β-methyl-*trans*-decal-2-one, m. p. 68—70°, kindly supplied by Professor A. J. Birch, gave a large depression of the m. p. The authentic *trans*-compound had $\nu_{max.}$ (liquid film) at 3500, 1706, 1452, 1420, 1152, 1072, 1024, 1000, 960, and 846 cm.$^{-1}$.

The *cis*-hydroxy-ketone (940 mg.) in acetone (20 ml.) was oxidised with 8N-chromic acid until there was a permanent orange colour. The solution was diluted with water and extracted with ether, and the organic layer washed with 5% sodium hydrogen carbonate solution and water and dried ($MgSO_4$). The residue, after removal of the solvent, crystallised from light petroleum–ether to afford the *cis*-dione (840 mg.), m. p. and mixed m. p. 64·5—65°.

Catalytic Reduction of 10β-*Methyl*-5β-*tetrahydropyranyloxy*-$\Delta^{1(9)}$-2-*octalone*.—The tetrahydropyranyl ether of 5β-hydroxy-10β-methyl-$\Delta^{1(9)}$-2-octalone was made by Jaeger's method.[6] It[6] had m. p. 65—66° (lit., 68—74°,[1] 62—64° [6]). The substance (3·3 g.) was hydrogenated over 2% palladium–strontium carbonate (350 mg.) in ethanol (30 ml.) at room temperature and pressure. After 20 min., uptake of hydrogen ceased at one mol. The solution was filtered and refluxed for 30 min. with dilute hydrochloric acid (5 ml.) under nitrogen. Extraction with ether followed by evaporation of the extract gave an oil which solidified (800 mg.) after trituration with light petroleum at −20°. Crystallisation from ether–light petroleum furnished 5β-hydroxy-10β-methyl-*cis*-decal-2-one, m. p. and mixed m. p. 64—65°. The mother-liquors, chromatographed on neutral alumina (Grade III, 60 g.), furnished some more (530 mg.) of the same compound, m. p. 67—68°.

Reduction of 9-*Methyl*-$\Delta^{5(10)}$-*octalin*-1,6-*dione by Lithium Aluminium Hydride*.—A solution of this dione (10 g.) in ether (250 ml.) was added during 30 min. to a stirred refluxing suspension of lithium aluminium hydride (6 g.) in ether. After 2 hr. the mixture was cooled and treated successively with ethyl acetate and dilute sulphuric acid. Extraction with ether followed by evaporation afforded a gum which was adsorbed on neutral alumina (250 g.; Grade IV) from ether. Elution with the same solvent gave gums which on trituration with ethyl acetate afforded 9β-*methyl*-$\Delta^{5(10)}$-*octalin*-1β,6β-*diol* (7·5 g.), m. p. 137—141°. Several recrystallisations from ethyl acetate raised the m. p. to 145—146° (Found: C, 72·3; H, 9·8. $C_{11}H_{18}O_2$ requires C, 72·5; H, 10·0%). The infrared spectrum (in Nujol) had main bands at 3335, 3000, 1662, 1322, 1292, 1264, 1060, 1046, 1030, 976, 928, and 860 cm.$^{-1}$. The *diacetate*, formed by treatment with acetic anhydride–pyridine overnight, crystallised from light petroleum as needles, m. p. 75° (Found: C, 67·5; H, 8·1. $C_{15}H_{22}O_4$ requires C, 67·6; H, 8·3%), $\nu_{max.}$ 1740 (OAc), 1240 (complex) cm.$^{-1}$.

Further elution with ether gave 9β-*methyl*-$\Delta^{5(10)}$-*octalin*-1β,6α-*diol* (1·7 g.), m. p. 126—129°, raised to 133—135° by several recrystallisations from ethyl acetate (Found: C, 72·5; H, 9·8%), $\nu_{max.}$ (in Nujol) 3340, 3000, 1660, 1322, 1284, 1056, 1028, 990, 912, and 858 cm.$^{-1}$. Attempts to prepare a diacetate yielded an impure substance as plates (from light petroleum), m. p. 84—85° Found: C, 70·3; H, 8·2%), $\nu_{max.}$ 1740 (OAc) and 1240 cm.$^{-1}$ (no OH absorption).

Hydrogenation of 9β-*Methyl*-$\Delta^{5(10)}$-*octalin*-1β,6β-*diol*.—The diol (750 mg.; m. p. 145—146°) in ethanol (25 ml.) was hydrogenated in the presence of 2% palladium–calcium carbonate (1 g.). After 1 hr., absorption of hydrogen ceased at 2 mols. Distillation of the residue, after removal of catalyst and solvent, gave 9β-methyl-*trans*-1β-decalol (670 mg.), b. p. 126°/14 mm., n_D^{17} 1·5040, $\nu_{max.}$ (liquid film) 3500, 1444, 1260, 1056, 1032, and 976 cm.$^{-1}$. The 3,5-*dinitrobenzoate* was obtained by heating the decalol and 3,5-dinitrobenzoyl chloride on a water-bath for 1 hr. The product was triturated with warm 5% sodium hydrogen carbonate solution and then crystallised from light petroleum (b. p. 60—80°). It had m. p. 133° (Found: C, 58·8; H, 6·0; N, 7·9. $C_{18}H_{22}O_6N_2$ requires C, 59·7; H, 6·1; N, 7·7%).

In a second experiment, the diol (3·2 g.) in ethanol (100 ml.) was hydrogenated at room temperature and pressure over 2% palladium–calcium carbonate (4 g.), but after 1·5 mols. had been absorbed the catalyst and solvent were removed and the remaining oil was distilled in distinct fractions: (*a*) b. p. 90°/0·5 mm., n_D^{17} 1·5035 (1·22 g.), which was redistilled to give an oil, b. p. 124—126°/15 mm., n_D^{18} 1·5037, whose infrared spectrum was identical with that of 9β-methyl-*trans*-1β-decalol; and (*b*) b. p. 114—118°/0·5 mm., which solidified after redistillation to give 9β-methyl-*trans*-decalin-1β,6β-diol, m. p. 133° (from ether) (Birch *et al.*[7] give m. p. 132—133°), $\nu_{max.}$ (in Nujol) 3400, 3000, 1266, 1072, 1046, 1028, 1008, 968, 940, and 912 cm.$^{-1}$.

The *trans*-decalol (920 mg.) [from (*a*)] in acetic acid (5 ml.) was treated with chromium trioxide (1 g.) in acetic acid (5 ml.) and water (0·5 ml.). After 1 hr. the mixture was diluted with water and extracted with ether. Distillation gave *trans*-9-methyl-1-decalone, b. p. 126°/18 mm. (Johnson [11] gives b. p. 119—120°/14—15 mm.). The 2,4-dinitrophenylhydrazone, in chloroform, after filtration through 4 : 1 bentonite–kieselguhr, crystallised from ethyl acetate–ethanol as orange plates, m. p. 168—169°, not depressed on admixture with the authentic *trans*-derivative, m. p. 169—170°, kindly supplied by Professor W. S. Johnson, but depressed to 143·5—145° on admixture with the *cis*-derivative, m. p. 164·5—165·5°. The infrared spectrum (chloroform solution) of the derivative was identical with that of the authentic *trans*-compound. The semicarbazone, which was formed readily at 0°, crystallised from methanol as blades, m. p. 218·5—219·5° (lit.,[11] m. p. 219—220°) (Found: C, 64·7; H, 9·2; N, 18·8. Calc. for $C_{12}H_{21}ON_3$: C, 64·5; H, 9·5; N, 18·8%).

A solution of 9β-methyl-*trans*-decalin-1β,6β-diol (850 mg.) in acetic acid (10 ml.) was treated with chromium trioxide (850 mg.) in acetic acid (5 ml.) and water (0·5 ml.). After 1 hr. the mixture was diluted with water and extracted with ether. Working up gave an oil (670 mg.), the bis-2,4-dinitrophenylhydrazone of which crystallised from chloroform–ethanol as an orange powder, m. p. 230° alone or mixed with the authentic *trans*-derivative, but 223—225° when mixed with *cis*-compound.

1,2,3,7,8,9-*Hexahydro*-1β-*hydroxy*-9β-*methylnaphthalene* (VI).—The crude mixture of 9β-methyl-$\Delta^{5(10)}$-decalin-1β,6β- and -1β,6α-diol [obtained by reduction of 6 g. of dione (I) by lithium aluminium hydride] was refluxed in dry benzene (100 ml.) with toluene-*p*-sulphonic acid monohydrate (100 mg.) under a Dean and Stark separator. After 2 hr. the mixture was cooled, washed with water, and dried ($MgSO_4$). Removal of the solvent at reduced pressure gave the *dienol* (3·50 g., 66%), b. p. 82°/0·1 mm., n_D^{17} 1·5480 (Found: C, 80·3; H, 9·8. $C_{11}H_{16}O$ requires C, 80·3; H, 9·8%), $\lambda_{max.}$ 235 mμ (ε 17,300).

Catalytic Reduction of the Dienol (VI).—The dienol (1·1 g.) in ethanol (50 ml.) was hydrogenated at room temperature and pressure over 2% palladium–strontium carbonate (1 g.). 2 Mols. of hydrogen were absorbed after 30 min. Removal of the catalyst, and then of the solvent at reduced pressure, gave 9β-methyl-*trans*-1β-decalol (1·0 g.), b. p. 128°/14 mm., n_D^{25} 1·4980. The 3,5-dinitrobenzoate, m. p. 134—135°, was identical with the specimen prepared as described on p. 2684.

1,2,3,7,8,9-*Hexahydro*-9-*methyl*-1-*oxonaphthalene*.—The dienol (VI) (1·32 g.) in acetone (20 ml.) was treated dropwise with 8N-chromic acid until there was a slight excess of reagent. Working up gave the dienone (620 mg.), b. p. 118—122°/15 mm., n_D^{25} 1·5060, $\lambda_{max.}$ 234 mμ (ε 14,600). The 2,4-*dinitrophenylhydrazone*, purified by chromatography in chloroform on 4 : 1 bentonite–kieselguhr, formed yellow needles (from ethanol), m. p. 145° (Found: C, 58·9; H, 5·3; N, 16·8. $C_{17}H_{18}O_4$ requires C, 59·6; H, 5·3; N, 16·4%). There was no trace of a red 2,4-dinitrophenylhydrazone.

1β,6-*Acetoxy*-1,2,3,7,8,9-*hexahydro*-9β-*methylnaphthalene*.—A solution of 5β-hydroxy-10β-methyl-$\Delta^{1(9)}$-2-octalone (2·9 g.) in benzene (75 ml.) was treated with toluene-*p*-sulphonic acid (100 mg.) and redistilled isopropenyl acetate (20 ml.), and the mixture was slowly distilled under a continuous take-off head. After 4 hr. and 6 hr., further portions of isopropenyl acetate (5 ml.) were added. The distillate was run into a solution of 2,4-dinitrophenylhydrazine in ethanolic sulphuric acid. After 7 hr., when the theoretical amount of acetone dinitrophenylhydrazone had been collected, the solvents were removed at reduced pressure. The residue was extracted with ether; distillation gave the acetate) 3·0 g., 86%), b. p. 120°/0·1 mm., $\lambda_{max.}$ 243 mμ, ε 18,000.

Reduction of the Enol Acetate.—The preceding acetate (2·75 g.) in glacial acetic acid (30 ml.) was added to a prehydrogenated suspension of platinum oxide (100 mg.) in the same solvent (20 ml.). 1, 2, and 3 mols. of hydrogen were absorbed after a total of 12, 30, and 120 min., respectively. After removal of the catalyst and solvent, distillation furnished a mixture of 1β-acetoxy-9β-methyl-*cis*- and -*trans*-decalin (2·05 g., 94%), b. p. 68°/0·15 mm., n_D^{20} 1·4760 (Found: C, 74·1; H, 10·2. Calc. for $C_{13}H_{22}O_2$: C, 74·2; H, 10·5%). The oil had a strong smell of camphor.

A solution of the mixed acetates (830 mg.) in ether was treated with lithium aluminium hydride, and the product oxidised with chromic acid in acetone. This oxidation product gave a 2,4-dinitrophenylhydrazone whose m. p. could not be raised above 134—142° (Found: C, 58·6; H, 6·1; N, 16·1. Calc. for $C_{17}H_{22}O_4N_4$: C, 58·9; H, 6·4; N, 16·2%), and a semicarbazone (needles from ethanol) whose m. p. could not be raised above 198—199° (Found: C, 64·2; H, 9·1. Calc. for $C_{12}H_{21}ON_3$: C, 64·5; H, 9·5%).

1,2,3,7,8,9-*Hexahydro*-6-*ethoxy*-9-*methyl*-1-*oxonaphthalene* (VII).—A mixture of 9-methyl-$\Delta^{5(10)}$-octalin-1,6-dione (8·64 g.), redistilled ethyl orthoformate (8·2 g.), and benzene (50 ml.) was treated with ethanol (1 ml.) and concentrated hydrochloric acid (2 drops). After 2 hours' refluxing the mixture was cooled, diluted with ether, washed with 5% sodium hydroxide solution and water, and dried ($MgSO_4$). Distillation yielded the enol ether (8·6 g., 86%), b. p. 100—102°/0·07 mm., n_D^{12} 1·5270. Swaminanthan and Newman [1] recorded b. p. 101—104°/0·1 mm., n_D^{25} 1·5257, but when the enol ether was made according to their directions the product was a complex mixture.

Catalytic Reduction of the Enol Ether (VII).—The pure ether (6·54 g.) in ethanol (50 ml.) was hydrogenated over 2% palladium–calcium carbonate (6 g.). Absorption of hydrogen ceased after 20 min. at 1 mol. Removal of catalyst and solvent, and distillation of the residue, gave 6-*ethoxy*-9-*methyl*-Δ^6-trans-1-*octalone* (5·4 g.), b. p. 102°/0·25 mm., n_D^{20} 1·4990 (Found: C, 74·4; H, 9·3. $C_{13}H_{20}O_2$ requires C, 75·0; H, 9·8%). Hydrolysis with boiling 2·5% ethanolic sulphuric acid under nitrogen for 1 hr. furnished pure 9-methyl-*trans*-decalin-1,6-dione in quantitative yield.

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