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TERPENOIDS—XCVIII

SYNTHESIS OF (±) 4-DEMETHYLDIHYDROEUDESMOL AND (±)-*trans*-5α,9β-DIMETHYL-2-DECALONE*

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Abstract—The title compounds have been synthesized. The Huang-Minlon reduction of ketoalcohol XVI has been studied. Improved methods for the preparation of 2-methylcyclohexane-1,4-dione and 4,4-ethylenedioxy-2-methylcyclohexanone have been developed.

THE relative stabilities of substituted *cis*- and *trans*-decalins depend on the nature of substituents and has been extensively investigated.[1] While equilibration of α-decalone XI furnishes[2] a mixture composed predominantly (90%) of the *trans*-isomer XII, equilibration of 10-methyl-1-decalone (XIII) furnishes[4] a mixture containing approximately equal amounts of the *cis* XIV and *trans* XV isomers. The Huang-Minlon reduction of 10-methyl-1-decalone (XIII) furnishes[3] an approximately 50:50 mixture of the *cis* II and *trans* I decalins.

It was considered of interest to extend this work to 10-methyl-1-decalones substituted at C_7. Huang-Minlon reduction[4] of the ketoalcohol XVI[5,6] obtained by ozonolysis of β-eudesmol XVII has been studied. The GLC behaviour of reduction product as well as the NMR spectrum showed that it is a mixture of two components. One of the components has been identified as the alcohol III by direct comparison with an authentic sample synthesized by the route given below. The structure of the other compound has not been rigorously established but it is tentatively assigned structure IV by analogy with the Huang-Minlon reduction products of 10-methyl-1-decalone (XIII).[4]

(±)-*cis*-10-Methyl-2-*trans*-decalol (V)[7] on treatment with PBr_3 furnished (±)-bromocompound VI. The stereochemistry at C_2 of the bromocompound VI has

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[1] E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis*, pp. 231 236. Interscience, New York (1965).

[2] H. E. Zimmerman and A. Mais, *J. Amer. Chem. Soc.*, **81**, 3664 (1959).

[3] It has been pointed out[4] that the relative quantities of decalins I and II formed during the reduction do not necessarily reflect the position of equilibrium of the decalones XIV and XV.

[4] F. Sondheimer and D. Rosenthal, *J. Amer. Chem. Soc.* **80**, 3995 (1958).

[5] [a] L. Ruzicka, A. H. Wind and D. R. Koolhaas, *Helv. Chim. Acta* **14**, 1132 (1931); [b] A. J. Birch and K. M. C. Mostyn, *Austr. J. Chem.* **7**, 301 (1954); [c] B. Reniker, J. Kalvoda, D. Arigoni, A. Furst, O. Jeger, A. M. Gold and R. B. Woodward, *J. Amer. Chem. Soc.* **76**, 313 (1954); [d] H. Hikino, Y. Hikino, Y. Takeshita, K. Megur and T. Takemato, *Chem. Pharm. Bull* (*Tokyo*) **11**, 1207 (1963); [e] V. B. Zalkow, A. M. Shaligram and L. H. Zalkow, *Chem. & Ind.* 195 (1965); [f] H. Hikino, Y. Hikino, Y. Takeshita, K. Meguro and T. Takemato, *Chem. Pharm. Bull* (*Tokyo*) **13**, 1408 (1965); [g] R. P. Houghton, D. C. Humber and A. R. Pinder, *Tetrahedron Letters* 353 (1966).

[6] A qualitative study of the relative stabilities of the *cis* (XVIA) and *trans* (XVI) ketoalcohols has been reported.[5a]

[7] R. H. Baker, L. S. Minckler and A. S. Hussey, *J. Amer. Chem. Soc.* **81**, 2379 (1959).

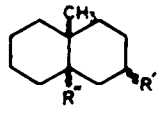
been assigned on the basis of analogy[8] and is further supported by its NMR spectrum which exhibits a narrow band (width at half height 8 c/s) at 4·66δ, characteristic for axial bromo compounds.[9] Treatment of the bromo compound VI with alcoholic KCN and alkaline hydrolysis of the resulting nitrile VII furnished the (±)-acid VIII[10] as a crystalline solid, m.p. 106–107°. Methyl ester X on treatment with MeMgI furnished (±)-alcohol III.

Many of the transformation products of naturally occurring eudesmanic compounds contain an equatorial methyl group at C_4.[12,13] With a view to systhesize some of these transformation products especially 4-epidihydro-eudes mol[12] and 4-epitetrahydro-alantolactone,[13] we have prepared (±)-*trans*-5α,9β-dimethyl-2-decalone XLIX employing the ketoketal XXVII[14] as the starting material.[15] The previously reported 2-methyl cyclohexane-1,4-dione XXVIII[14,20] has been prepared in excellent yields by hydrogenating *o*-toluquinone XX at 150° and 150 atm to the diol XXI (possibly a mixture of stereoisomers) and subsequent oxidation with Jones reagent.[21] Reaction of diketone XXVIII with 1 mole of ethylene glycol resulted in the selective ketalization of C_4 carbonyl group to furnish ketoketal XXVII.

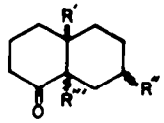
In an alternate approach, diol XXI was benzoylated to furnish dibenzoate XXII as a crystalline solid. Hydroxybenzoate XXIII prepared by controlled saponification of XXII was converted to ketoketal XXVII employing the route XXIII → XXIV → XXV → XXVI → XXVII.

Condensation of ketoketal XXVII with 1-chloropentane-3-one in presence of sodium hydride[22] and base treatment of the resulting product furnished 6,6-ethylenedioxy-1-10β-dimethyl $\Delta^{1,(9)}$-octal-2-one XLII, in satisfactory yields. Reduction of octalone XLII with lithium and ethanol in liquid ammonia followed by CrO_3–pyridine oxidation[23] furnished *trans*-decalone XLV. The stereochemistry assigned to decalone XLV is based on generally accepted reaction mechanisms of metal ammonia reduction of α,β-unsaturated ketones[17,24] and also by analogy with reduction

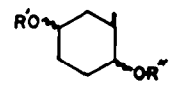
[8] G. Roberts, C. W. Shoppee and R. J. Stephenson, *J. Chem. Soc.* 2705 (1954).
[9] N. S. Bhacca and D. H. Williams, *Applications of NMR Spectroscopy in Organic Chemistry*, p. 74 Holden-Day (1964).
[10] After we had completed the preparation of (±)-acid VIII, its synthesis was published.[11]
[11] J. A. Marshall and M. T. Pike, *Tetrahedron Letters* No. 35, 3107 (1965).
[12] E. Von Rudloff and H. Erdtman, *Tetrahedron* **18**, 1315 (1962).
[13] K. Tanabe, *Chem. Pharm. Bull. (Tokyo)* **6**, 218 (1958).
[14] S. A. Narang and P. C. Dutta, *J. Chem. Soc.* 2842 (1960).
[15] Condensation of vinyl ethyl ketone with ketoalcohol XXX or methyl ether XXXI did not appear promising; condensation of vinyl methyl ketone with XXX is reported to give bicyclic alcohol XXXII in poor yield[16] and the reaction of vinyl methyl ketone with ether XXXI furnishes an epimeric mixture of octalones XXXIII and XXXIV.[17] Recently bicyclic ketones XXXV and XXXVI have been prepared and are the key intermediates for the synthesis of alantolactone XXXVII[18] and isoalantolactone XXXVIII[19] respectively.
[16] F. Sondheimer and Deo Elad, *J. Amer. Chem. Soc.* **79**, 5542 (1957).
[17] G. Stork and S. D. Darling, *J. Amer. Chem. Soc.* **86**, 1761 (1964).
[18] J. A. Marshall and Noal Cohen, *J. Amer. Chem. Soc.* **87**, 2773 (1965).
[19] H. Minato and I. Horibe, *Chem. Commun.* 531 (1965).
[20] R. M. Lukes, G. I. Poos and L. H. Sarett, *J. Amer. Chem. Soc.* **74**, 1401 (1952).
[21] K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* 39 (1946).
[22] T. G. Halsall, D. W. Theobald and K. B. Walshaw, *J. Chem. Soc.* 1029 (1964).
[23] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Amer. Chem. Soc.* **75**, 422 (1953).
[24] M. J. T. Robinson, *Tetrahedron* **21**, 2475 (1965).



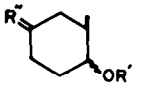
I $R' = H$, $R'' = \alpha\text{-}H$
II $R' = H$, $R'' = \beta\text{-}H$
III $R' = \beta\text{-}C(CH_3)_2OH$, $R'' = \alpha\text{-}H$
IV $R' = \beta\text{-}C(CH_3)_2OH$, $R'' = \beta\text{-}H$
V $R' = \beta\text{-}OH$, $R'' = \alpha\text{-}H$
VI $R' = \alpha\text{-}Br$, $R'' = \alpha\text{-}H$
VII $R' = \beta\text{-}CN$, $R'' = \alpha\text{-}H$
VIII $R' = \beta\text{-}COOH$ $R'' = \alpha\text{-}H$
IX $R' = \alpha\text{-}CN$, $R'' = \alpha\text{-}H$
X $R = \beta$ $COOMe$, $R'' = \alpha\text{-}H$



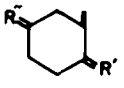
XI $R' = R'' = R''' = H$
XII $R' = R'' = H$, $R''' = \alpha\text{-}H$
XIII $R' = CH_3$, $R'' = R''' = H$
XIV $R' = CH_3$, $R'' = H$, $R''' = \alpha\text{-}H$
XV $R' = CH_3$, $R'' = H$, $R''' = \beta\text{-}H$
XVI $R' = CH_3$, $R'' = \beta\text{-}C(CH_3)_2OH$, $R''' = \alpha\text{-}H$
XVIA $R' = CH_3$, $R'' = \beta\ C(CH_3)_2OH$, $R''' = \beta\text{-}H$



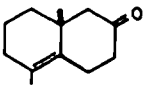
XXI $R' = R'' = H$
XXII $R' = R'' = CO\cdot\phi$
XXIII $R' = H$, $R'' = CO\cdot\phi$



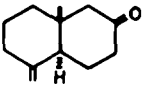
XXIV $R' = CO\cdot\phi$, $R'' = O$
XXV $R' = CO\cdot\phi$, $R'' = $ 
XXVI $R' = H$, $R'' = $



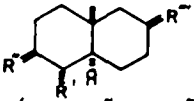
XXVII $R' = O$, $R'' = $ 
XXVIII $R' = R'' = O$
XXIX $R' = R'' = $ 
XXX $R' = O$, $R'' = $
XXXI $R' = O$, $R'' = $ 



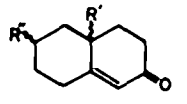
XXXV



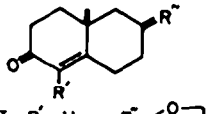
XXXVI



XLIV $R' = H$, $R'' = O$, $R''' = $
XLV $R' = CH_3$, $R'' = O$, $R''' = $
XLVI $R' = H$, $R'' = H_2$, $R''' = $
XLVII $R' = CH_3$, $R'' = H_2$, $R''' = $
XLVIII $R' = H$, $R'' = H_2$ $R''' = O$
XLIX $R' = CH_3$, $R'' = H_2$, $R''' = O$



XXXII $R' = \beta\text{-}CH_3$, $R'' = OH$
XXXIII $R' = \beta\text{-}CH_3$, $R'' = \beta\text{-}OCH_3$
XXXIV $R' = \alpha\text{-}CH_3$, $R'' = \beta\text{-}OCH_3$



XLI $R' = H$, $R'' = $ 
XLII $R' = CH_3$, $R'' = $ 
XLIII $R' = H$, $R'' = O$

of conjugated ketones of similar structure such as 4-methyl-cholestenone[25] 3-oxo-eudesm-4-en-13-oic acid[26] XXXIII, XXXIV[17] and particularly the ketoketal XLI whose preparation and reduction are discussed below. Decalone XLV on Huang-Minlon reduction to XLVII and subsequent deketalization furnished (±)-*trans*-5α-9β-dimethyl-2-decalone XLIX.

α,β-Unsaturated ketone XLI was prepared by the Robinson annelation on ketoketal XXVII and was converted to diketone XLIII. Octalone XLI furnished *trans*-decalone XLIV on reduction with lithium and alcohol in liquid ammonia followed by CrO_3–pyridine oxidation. Rigorous proof of the *trans* stereochemistry of decalone XLIV was provided by its conversion to *trans*-decalone XLVIII[27] employing the sequence XLIV → XLXI → XLVIII. *trans*-Decalone XLVIII thus prepared yielded *trans*-1-methylcyclohexane-1,2-diacetic acid (L)[28] on nitric acid oxidation.

[25] Y. Mazur and F. Sondheimer, *J. Amer. Chem. Soc.* **80**, 5220 (1958).
[26] K. S. Kulkarni and A. S. Rao, *Tetrahedron* **21**, 1167 (1965).
[27] [a] W. Nagata and I. Kikkawa, *Chem. Pharm. Bull (Tokyo)* **11**, 289 (1963); [b] C. Djerassi and J. E. Gurst, *J. Amer. Chem. Soc.* **86**, 1755 (1964); [c] J. A. Marshall and Ronnie D. Carroll, *J. Org. Chem.* **30**, 2748 (1965).
[28] R. L. Kronenthal and E. I. Becker, *J. Amer. Chem. Soc.* **79**, 1095 (1957).

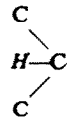
EXPERIMENTAL

All m.ps and b.ps are uncorrected. Elemental analyses are due to Mr. Pansare and colleagues of our laboratory. IR (Perkin-Elmer spectrophotometer). UV (Beckman DK-2 spectrophotometer). NMR (Varian A60 instrument in CCl_4 with TMS as internal ref.) by I. Mulla. GLC (Griffin VPC apparatus MK IIA). We thank Dr. B. B. Ghatge for providing VPC data of our compds.

Huang-Minlon reduction of ketoalcohol (XVI). Commercial "eudesmol"† was chromatographed on a column of alumina (grade II; ratio of alumina:substrate 30:1). The column was eluted successively with pet.ether, pet.ether–benzene mixture and benzene. The material eluted with benzene consists of a mixture of α- and β-eudesmol and had $[\alpha]_D$ +27° (*c*, 3·0; $CHCl_3$). GLC examination showed two peaks in the ratio of 28:72; retention time 3·0 and 3·83 min respectively, using a polyester column, temp 218° and H_2 as carrier gas (flow rate 75 ml/min.). This mixture was used as such.

The mixture of α- and β-eudesmol (3·2 g) was dissolved in chf (40 ml). Ozone was passed through the cooled soln (0°) for 75 min. (rate of ozone 0·8 g/hr). H_2O_2 (30%) (7 ml) and AcOH–water (1:1) (15 ml) were added to the soln and the reaction mixture was kept overnight at room temp. The chf layer was washed with water and concentrated *in vacuo*. Water (10 ml) was added and the reaction mixture was heated on a water bath for 3 hr. The product was taken up in ether and washed with 10% Na_2CO_3 aq and water. The ether layer was dried and the solvent removed to furnish XVI (2·7 g) as an oily residue.

A mixture of XVI (0·32 g), 80% hydrazine hydrate (2 ml) and freshly distilled diethylene glycol (10 ml) was heated at 120° (bath) in N_2 atm. After 3 hr KOH pellets (1·0 g) were added to cooled reaction mixture, condenser was removed and temp of bath was raised slowly to 210° (bath). Condenser was replaced and temp maintained at 210° for 3 hr. The reaction mixture was diluted with water and extracted with ether (25 × 2 ml). The extract was washed with water, dried and the solvent removed to furnish a viscous oil (0·177 g) b.p. 120–130° (bath)/0·2 mm, $[\alpha]_D$ +7° (*c*, 2·45 chf) (Found: C, 79·12; H, 12·08. $Cl_4H_{26}O$ requires: C, 79·93; H, 12·46%.) IR (liquid film): 3400, 1480, 1465, 1395, 1160, 955 and 918 cm^{-1}. GLC of this oil exhibited two peaks (retention time 2·06 and 2·7 min respectively; polyester column, temp 218°, H_2 as carrier gas, (flow rate, 75 ml/min). NMR 0·79 δ (s; 1·5 H; angular CH_3 in III), 0·83 δ (s; 1·5 H, angular CH_3 in IV), 1·12 δ (s; 6H; $C{\cdot}C(CH_3)_2OH$).

(+)-trans-trans-2-*Bromo*-10-*methyldecalin* (VI). Freshly distilled PBr_3 (1 ml) was added to a cooled (±)-*cis*-10-methyl-2-*trans*-decalol (V) (1·8 g). The reaction mixture was kept at room temp under anhyd conditions for 18 hr, warmed on a water bath for ½ hr, poured on to crushed ice (25 g) and the product extracted with ether (25 × 2 ml). The extract was washed with water, dried and on removal of the solvent VI (1·698 g) was obtained as a colourless liquid, b.p. 100–115° (bath)/1·5 mm, n_D^{26} 1·5152 [Found: C, 58·91; H, 8·40. $C_{11}H_{19}Br$ requires: C, 57·13; H, 8·26. (The higher carbon value may be due to the presence of small quantities of elimination products).] IR (liquid film): 1460, 1390, 1368, 1275, 1265, 1246, 1205, 996, 965, 860 and 700 cm^{-1}. NMR: 0·78 δ (s; 3H; angular CH_3), a narrow band at 4·66 δ (height at half width 8 c/s; 1 H; ).

(±)-trans-cis-10-*methyldecalin*-2-*carboxylic acid* (VIII). (A) A mixture of VI (1·548 g), EtOH (50 ml) and KCN (1·1 g) was refluxed for 24 hr, cooled, diluted with water and extracted with ether. The extract was dried and the solvent removed to furnish a mixture of (±)-*trans-cis*-2-cyano-10-methyldecalin(VII) and elimination products as a colourless liquid (0·99 g), b.p. 75–90° (bath)/1·2 mm.

The mixture (0·83 g) was refluxed with 10% alcoholic KOH (50 ml) for 22 hr, concentrated, diluted with water, extracted with ether, and the extract rejected. The aq layer was acidified with cold HCl (1:1) and the liberated acid was extracted with ether (25 × 2 ml). The extract was washed with water, dried and on removal of the solvent, a solid residue (0·11 g) was obtained. Crystallization from pet ether (60–80°) afforded pure VIII, m.p. 106–107°.

(B) A mixture of *p*-toluenesulphonate of (±) *cis*-10-methyl-2-*trans*-decalol (V)' (0·38 g), dimethylformamide (22 ml), t-BuOH (12 ml) and KCN (0·71 g) was heated at 140° for 15 hr. The

† Commercial "eudesmol" was purchased from Plaimar Ltd., Australia. A systematic investigation of this commercial eudesmol has been carried out by E. von Rudloff [*Chem. & Ind.*, 743 (1962)].

reaction mixture was worked up as described under (A) to furnish a mobile liquid (0·23 g) of (±)-*trans-trans*-2-cyano-10-methyldecalin (IX) mixed with elimination products.

The above liquid (0·23 g) was refluxed with 5% glycolic KOH (20 ml) for 6 hr. On working up the reaction mixture as described under (A) VIII (0·071 g) was obtained, m.p. 106–107° after sublimation [95–105 (bath)/0·8 mm] and crystallization from pet ether(60–80°).

The m.m.p. of the (±)-acid VIII prepared by methods A and B was 106–107°.

(±)-4-*Demethyldihydroeudesmol* (III). The methyl ester (X) (85 mg) [prepared from VIII (100 mg) by diazomethane method] in anhyd. ether (10 ml) was added dropwise to a cooled (0°) Grignard reagent prepared from Mg (0·25 g) and MeI (2·5 ml). The reaction mixture was refluxed for 3 hr cooled, decomposed with sat., NH_4Cl aq, and the product extracted with ether. The extract was washed with water, dried and on removal of solvent furnished III (70 mg) as a viscous liquid, b.p. 130–35° (bath)/0·6 mm. (Found: C, 80·23; H, 12·53. $C_{14}H_{26}O$ requires: C, 79·93; H, 12·46%.) IR (liquid film): 3400, 1480, 1465, 1392, 1160, 1000, 950, 918 and 820 cm^{-1}. GLC: a single peak (retention time 2·7 min, polyester column, temp 218°, H_2 as carrier gas). NMR: 0·78 δ (s, 3H, angular CH_3), 1·12 δ (s, 6H, $C{\cdot}C(CH_3)_2OH$).

Hydrogenation of o-*toluquinone* (XX). Compound XX (21·7 g) was hydrogenated in EtOH (50 ml) in presence of Raney Ni (6·0 g) at 150° and 150 atm. The catalyst was filtered off, EtOH removed and the residue distilled to furnish 2-methylcyclohexane-1,4-diol (XXI) (17·8 g) as a viscous liquid. IR (liquid film): 3448, 1451, 1418, 1370, 1220, 1098, 1053, 1030, 1010, 978, 952, 927, 885 and 847 cm^{-1}.

2-*Methylcyclohexane*-1,4-*dione* (XXXIII). Compound XXI (1·0 g) in acetone (40 ml) was oxidized with Jones reagent with cooling. After destroying the excess reagent with MeOH, the reaction mixture was concentrated, diluted with water, and extracted with ether. The ether extract was washed with 5% $NaHCO_3$ aq and water, and dried. On removal of the solvent 2-methylcyclohexane, 1,4-dione (XXVIII) was obtained (0·65 g) which was crystallized from pet. ether (60–80°), m.p. 46–47° (lit.[14,39] m.p. 47–48°). (Found: C, 66·55; H, 7·79. $C_7H_{10}O_2$ requires: C, 66·64; H 7·99%.)

4,4-*Ethylenedioxy*-2-*methylcyclohexanone* (XXVII). 2-Methylcyclohexane-1,4-dione (XXVIII) (0·37 g), ethylene glycol (0·167 g) (1 mol) and *p*-toluenesulphonic acid (25 mg) were refluxed in benzene (50 ml) for 6 hr and the water produced during the reaction was suitably trapped. The reaction mixture was washed with $NaHCO_3$ aq and water, and benzene removed. The residue on distillation furnished XXVII (0·25 g), b.p. 110–120° (bath)/1·5 mm. (Found: C, 63·10; H, 7·85. $C_9H_{14}O_3$ requires: C, 63·51; H, 8·29%.) IR (liquid film): 1718, 1453, 1366, 1307, 1290, 1242, 1143, 1124, 1092, 1057, 1022, 990, 952, 930 and 826 cm^{-1}.

1,1-4,4-*Diethylenedioxy*-2-*methylcyclohexane* (XXIX). (A) A mixture of XXVIII (0·46 g), *p*-toluenesulphonic acid (30 mg) and 2-ethyl-2-methyl-1,3-dioxolane (10 ml) was refluxed for 2 hr. The reaction mixture was diluted with benzene, washed with 5% $NaNCO_3$ aq and water. Benzene and 2-ethyl-2-methyl-1,3-dioxolane were removed using a vigreoux column. The residue on distillation furnished XXIX (0·55 g), b.p. 110–115° (bath)/0·8 mm. (Found: C, 61·81; H, 8·61. $C_{11}H_{18}O_4$ requires: C, 61·66; H, 8·47%.)

(B) 2-Methylcyclohexane-1,4-dione XXVIII (0·45 g), ethylene glycol (1·9 g) and *p*-toluenesulphonic acid (46 mg) were refluxed in toluene (50 ml) for 6 hr. The reaction mixture was washed with Na_2CO_3 aq and water. Toluene was removed *in vacuo* and distillation of the residue furnished XXIX (0·52 g), b.p. 120–130°/1·5 mm. (Found: C, 61·86; H, 8·5. $C_{11}H_{18}O_4$ requires: C, 61·66; H, 8·47%.) IR (liquid film): 1447, 1379, 1351, 1325, 1275, 1250, 1227, 1208, 1156, 1124, 1096, 1070, 1045, 1026, 985, 957, 934, 908, 814, 780 and 684 cm^{-1}.

1,4-*Dibenzoyloxy*-2-*methylcyclohexane* (XXII). BzCl (7 ml) was added to a cooled soln of XXI (3·5 g) in anhyd. pyridine (10 ml) and kept at room temp for 24 hr. The reaction mixture was poured on to crushed ice (30 g), extracted with ether. The extract was washed with dil HCl, 5% Na_2CO_3 aq and water, and dried. The solvent was distilled off and the residue was passed on a column of alumina (50 g, gr.II). Pet. ether eluted fraction (4·3 g) was obtained as solid, which after two crystallisations from pet. ether (60–80°), furnished XXII, m.p. 106–107°. (Found: C, 74·78; H, 6·67. $C_{21}H_{22}O_4$ requires: C, 74·53; H, 6·53%.) IR (in nujol): 1706, 1592, 1575, 1449, 1370, 1312, 1295, 1285, 1250, 1176, 1111, 1082, 1065, 1025, 990, 925 and 708 cm^{-1}.

4-*Benzoyloxy*-3-*methylcyclohexanone* (XXIV). Compound XXII (1·225 g) was refluxed with 4% ethanolic KOH (5 ml) (1 mol) for 6 hr. The reaction mixture was diluted with water and extracted

with ether. The extract was washed with water, dried and on removal of solvent 4-benzoyloxy-3-methylcyclohexanol (XXIII) (0·8 g) was obtained as an oil. IR (liquid film): 3497, 1712, 1603, 1583, 1493, 1366, 1274, 1176, 1111, 1070, 1027, 990, 925, 757 and 710 cm^{-1}.

Compound XXIII (0·75 g) on oxidation with Jones reagent furnished XXIV (0·7 g), b.p. 150–55° (bath)/4 mm. (Found: C, 72·02; H, 7·07. $C_{14}H_{16}O_3$ requires: C, 72·39; H, 6·94%.) IR (liquid film): 1724, 1610, 1587, 1449, 1418, 1360, 1316, 1280, 1176, 1114, 1070, 1020, 994, 948, 927, 865, 855, 810 and 714 cm^{-1}.

4,4-*Ethylenedioxy-2-methyl-cyclohexanol* (XXVI). Compound XXIV (0·7 g) was ketalized with ethylene glycol (0·95 g) in benzene (50 ml) in the presence of *p*-toluenesulphonic acid (22 mg) to furnish 1-benzoyloxy-2-methyl-4,4-ethylenedioxy cyclohexane (XXV) (0·72 g). IR (liquid film): 1724, 1610, 1587, 1450, 1360, 1342, 1316, 1280, 1176, 1160, 1114, 1070, 1020, 994, 927, 880, 803 and 714 cm^{-1}.

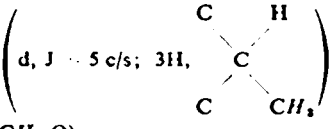
Compound XXV (0·72 g) on saponification with 4% alcoholic KOH (20 ml) in N_2 atm for 6 hr furnished XXVI (0·32 g), b.p. 110–115° (bath)/3 mm. (Found: C, 62·59; H, 9·27. $C_9H_{16}O_3$ requires: C, 62·76; H, 9·36%.) IR (liquid film): 3448, 1449, 1370, 1292, 1220, 1147, 1111, 1042, 975, 948, 925, 892, 847, 797 and 763 cm^{-1}.

4,4-*Ethylenedioxy-2-methylcyclohexanone* (XXVII). Compound XXVI (0·31 g) in anhydrous pyridine (5 ml) was added to CrO_3-pyridine complex [prepared from CrO_3 (500 mg) and pyridine (5 ml)] and kept at room temp overnight. The reaction mixture was diluted with water and extracted with ether (25 × 3 ml). The extract was washed with water, dried and the solvent removed. The residue on distillation furnished XXVII (0·116 g), b.p. 125–135° (bath)/1·5 mm. (Found: C, 63·22; H, 8·51. $C_9H_{14}O_3$ requires: C, 63·51; H, 8·29%.) IR (liquid film): 1718, 1453, 1366, 1307, 1290, 1242, 1143, 1124, 1092, 1057, 1022, 990, 952, 930 and 826 cm^{-1}; identical with that of an authentic sample prepared by lit.[14] method. GLC (polyester column, temp 220°, H_2 as carrier gas): a single peak (retention time 3·2 min.) identical with the sample prepared by lit.[14] method.

(±)-6,6-*Ethylenedioxy*-1,10-*Dimethyl*-$\Delta^{1(10)}$-*octal*-2-*one* (XLII). NaH (0·6 g) (washed with dry pet. ether) was added to XXVII (2·4 g) dissolved in anhyd. THF (10 ml) and the reaction mixture was stirred and refluxed in N_2 atm for 2 hr. 1-Chloropentan-3-one (2·0 g) was added dropwise to the cooled (0°) reaction mixture and stirring was continued for 2 hr at room temp. NaH was decomposed with water and the product extracted with ether. The extract was washed and dried. The residue obtained after removal of solvent was refluxed with 5% methanolic KOH (50 ml) for 6 hr in N_2 atm. It was concentrated to a small volume, diluted with water and extracted with ether. The extract was washed and dried. The residue obtained after ether removal (2·9 g) was fractionally distilled. (i) Fraction b.p. 110–140° (bath)/1 mm, 0·6 g, was identified as XXVII by comparative GLC analysis. (ii) Fraction b.p. 140–160° (bath)/1 mm, 0·91 g, solidified, pure XLII, m.p. 60–61°, was obtained after crystallization from pet. ether (40–60°) (Lit.[14] m.p. 61°). (Found: C, 71·42; H, 8·70. $C_{14}H_{20}O_3$ requires: C, 71·16; H, 8.53%.) UV (MeOH): 244 mμ (ε 14,000).

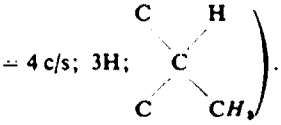
(±)-6,6-*Ethylenedioxy*-trans-1α,10β-*dimethyl*-2-*decalone* (XLV). Compound XLII (0·318 g) in ether (10 ml) was added dropwise to a soln of Li (0·2 g) in liquid NH_3 (100 ml) and stirred for 1 hr and then treated with EtOH (10 ml). The residue left after the evaporation of NH_3 was diluted with water and extracted with ether. The extract was washed and dried. The residue obtained after solvent removal was oxidised with CrO_3-pyridine to furnish XLV (0·2 g), b.p. 160–165° (bath)/4 mm (Found: C, 71·11; H, 9·47. $C_{14}H_{22}O_3$ requires: C, 70·55; H, 9·31%.) IR (liquid film): 1716, 1460, 1430, 1345, 1140, 1100, 1080, 1040, 1025, 1000, 985, 955, 930, 865, 840 and 785 cm^{-1}.

(±)-2,2-*Ethylenedioxy*-trans-5α,9β-*dimethyl*-*decalin* (XLVII). Compound XLV (0·16 g) on Huang-Minlon reduction furnished XLVII (0·115 g), b.p. 120–125° (bath)/1·5 mm. (Found: C, 75·11; H, 10·88. $C_{14}H_{22}O_2$ requires: C, 74·95; H, 10·78%.) IR (liquid film): 1470, 1400, 1370, 1280, 1225, 1190, 1165, 1106, 1000, 980, 965, 938, 930, 895, 840, 785 and 692 cm^{-1}. NMR: 0·82 δ



d, J ~ 5 c/s; 3H, 0·93 δ (s; 3H, angular CH_3), 3·77, 3·81, 3·85 δ (4H; $-O-CH_2-CH_2-O$).

(±)-trans-5α,9β-*Dimethyl*-2-*decalone* (XLIX). Compound XLVII (0·1 g) in acetone (40 ml) containing a few drops of water and *p*-toluenesulphonic acid (30 mg) was refluxed for 3 hr, concentrated and extracted with ether. The extract was washed with 5% $NaHCO_3$ aq and water, and

dried. The residue obtained after evaporation of ether on distillation furnished XLIX, b.p. 100–105° (bath)/1·5 mm. (Found: C, 80·46; H, 11·46. $C_{12}H_{20}O$ requires: C, 79·94; H, 11·48%.) IR (liquid film): 1715, 1465, 1435, 1390, 1365, 1300, 1245, 1220, 1200, 1175, 1130, 1068, 970, 862, 780 and 720 cm^{-1}. NMR: 0·79 δ (s; 3H; angular CH_3), 0·9 δ (d, $J \simeq 4$ c/s; 3H; ).

(±)-6,6-*Ethylenedioxy*-10-*methyl*-$\Delta^{1(9)}$-2-*octalone* (XLI). Methyl vinyl ketone (1·4 g) was added during 1/2 hr to a cooled (0°) and stirred soln of XXVII (2·5 g) and 3N EtONa (0·3 ml) in N_2 atm. After addition, the reaction mixture was kept at 0° for additional 6 hr, diluted with brine and extracted with ether. The extract was washed and dried. The residue obtained on removal of solvent was refluxed with 10% KOH aq (45 ml) in N_2 atm for 6 hr, and the product extracted with ether. The extract was washed with brine, and dried. The residue on removal of solvent was fractionally distilled to furnish (i) b.p. 100–140° (bath)/0·08 mm (0·9 g), identified as XXVII by GLC analysis; (ii) 140–180° (bath)/0·08 mm (0·72 g), m.p. 85–86°. On crystallization from pet. ether, pure XLI m.p. 91–92° was obtained. (Found: C, 70·06; H, 7·85. $C_{13}H_{18}O_3$ requires: C, 70·24; H, 8·18%.) UV (EtOH): 234 mμ (ε 17,400). IR (in nujol): 1660, 1613, 1449, 1429, 1361, 1328, 1287, 1233, 1224, 1193, 1179, 1157, 1136, 1117, 1075, 1028, 1020, 993, 956, 943, 877, 826, 790, 770, 726 and 707 cm^{-1}. NMR: 1·35 δ (s; 3H, angular CH_3), 3·88, 3·95, 3·98 δ (4H; —O—CH_2–CH_2—O), 5·64 δ (d, $J \simeq 2$ c/s; 1H, vinyl proton).

(±)-10-*Methyl*-$^{1(9)}$-*octalin*-2,6-*dione* (XLIII). Compound XLI (0·1 g) on deketalization in aq acetone in the presence of *p*-toluenesulphonic acid furnished XLIII (0·066 g) as solid which crystallized from pet. ether (40–60°) as needles m.p. 74–75°. (Found: C, 74·25; H, 8·01. $C_{11}H_{14}O_2$ requires: C, 74·13; H, 7·92%.) UV (EtOH): 234 mμ (ε 18,880). IR (in nujol): 1709, 1667, 1613, 1449, 1408, 1379, 1359, 1312, 1299, 1250, 1176, 1156, 1026, 979, 950, 938, 885, 862 and 769 cm^{-1}.

(±)-6,6-*Ethylenedioxy*-trans-10-*methyl*-2-*decalone* (XLIV). Compound XLI (0·327 g) on reduction with Li and EtOH in liquid NH_3 followed by CrO_3–pyridine oxidation of the resulting mixture furnished XLIV (0·305 g), b.p. 140–45° (bath)/0·8 mm. (Found: C, 69·69; H, 9·09. $C_{13}H_{20}O_3$ requires: C, 69·61; H, 8·99%.) IR (liquid film): 1709, 1447, 1418, 1379, 1361, 1316, 1282, 1253, 1147, 1089, 1070, 1045, 1036, 1010, 990, 970, 943, 925, 862 and 830 cm^{-1}.

(±)-2,2-*Ethylenedioxy*-trans-9-*methyl*-*decalin* (XLVI). Compound XLIV (0·29 g) on Huang-Minlon reduction furnished XLVI (0·19 g), b.p. 107–110° (bath)/0·7 mm. (Found: C, 74·59; H, 10·59. $C_{13}H_{22}O_2$ requires: C, 74·25; H, 10·59%.) IR (liquid film): 1449, 1357, 1316, 1262, 1233, 1176, 1167, 1149, 1095, 1078, 1047, 1015, 1004, 985, 950, 934, 893, 885 and 833 cm^{-1}.

(±)-trans-9-*Methyl*-2-*decalone* (XLVIII). Compound XLVI (0·18 g) on deketalization in aq acetone (30 ml) in the presence of *p*-toluenesulphonic acid (32 mg) furnished XLVIII (93 mg), b.p. 85–90° (bath)/0·5 mm. (Found: C, 79·36; H, 10·96. $C_{11}H_{18}O$ requires: C, 79·46; H, 10·92%.) IR (liquid film): 1710, 1445, 1397, 1374, 1350, 1307, 1282, 1227, 1181, 1160, 1149, 1114, 983, 938, 892, 848 and 763 cm^{-1}. NMR: 0·77 δ (s, 3H; angular CH_3).

HNO_3 *oxidation of* XLVIII. Compound XLVIII (0·11 g) was stirred with conc. HNO_3 at room temp for 2 hr. HNO_3 was evaporated off and the solid residue (0·056 g), after two crystallizations from AcOH furnished (±)-*trans*-1-methylcyclohexane-1,2-diacetic acid (L), m.p. 196–97°, no depression in m.p. on admixture with an authentic sample of L prepared from (±)-*trans*-10-methyl-2-decalone.[28]

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