879. *Some Preliminary Synthetical Studies with* 5,6,7,8-*Tetrahydro*-8-*methylindane*-1,5-*dione.*

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

Some reactions of the compound (I) named in the title have been investigated, principally with a view to setting up a *trans*-ring junction. Certain steroid analogues with a *cis*-fusion of the C/D rings have been prepared.

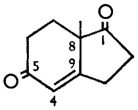
If a hexahydroindane is to serve as an intermediate in a steroid synthesis, it is vital that a *trans*-junction of the rings shall be incorporated in the intermediate or derivable at some future stage. It is of advantage to start with a saturated compound of the correct stereochemistry for proof of stereochemistry may be difficult at a later stage. Compound (I) is an obvious steroid intermediate [1] and its reduction has been studied with the intention of using the information so gained on 4-substituted derivatives.

Treatment of the dione (I) in ethanol with an equivalent amount of sodium borohydride gave an oil (82% yield) which was shown to be homogeneous by chromatography.

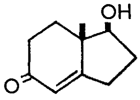
---

[1] (*a*) Acklin, Prelog, and Prieto, *Helv. Chim. Acta*, 1958, **41**, 1416; (*b*) Boyce and Whitehurst, *J.*, 1959, 2022.

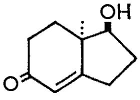
Ultraviolet light absorption ($\lambda_{max.}$ 242 mμ; ε 11,200) and the formation of a scarlet dinitrophenylhydrazone showed the conjugated enone system to be intact. The reduction was therefore both selective and stereospecific, and by analogy with the reduction of 17-ketosteroids [2] it was expected that the product was the (racemic) (β-)alcohol (II). At this point Prelog and Acklin [3] showed that the microbiological reduction of the dione (I) gave the optically active alcohols (II) and (III) (absolute configurations as depicted). Through the kindness of Professor Prelog and Dr. Acklin we were able to compare their products with ours. The infrared absorption of our ketol was identical with that of Prelog and Acklin's (II) but significantly different, especially in the 1350—1200 cm.$^{-1}$ and the 1080—1000 cm.$^{-1}$ regions, from that of the stereoisomer (III). Our compound was therefore the racemic form of (II).



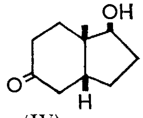
(I)



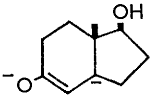
(II)



(III)



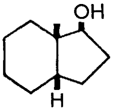
(IV)



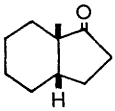
(V)

Lithium–ammonia reduced the alcohol (II) to a waxy solid (IV) (2,4-dinitrophenylhydrazone, m. p. 155—156°). It was expected that this was the *cis*-compound as the anion (V) should be more stable in the *cis*- than in the *trans*-form.[4]

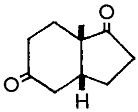
It was then found that catalytic reduction of the ketol (II) gave a saturated ketol; this was at first erroneously thought to be the desired *trans*-compound as its 2,4-dinitrophenylhydrazone melted at 133°. However, Wolff–Kishner reduction furnished the alcohol (VI) which was oxidised to the *cis*-ketone (VII), derivatives of which were identical with those of an authentic specimen [5] kindly provided by Professor W. S. Johnson (Wisconsin). Oxidation of the *cis*-ketol (IV) gave the *cis*-diketone (VIII), which was also obtained directly from our starting material (I) by catalytic reduction. Re-examination of the product of the lithium–ammonia reaction showed it to be identical with that of hydrogenation. The 2,4-dinitrophenylhydrazone of m. p. 156° melted at 133° after repeated crystallisation: polymorphism of 2,4-dinitrophenylhydrazones is, of course, well known.[6]



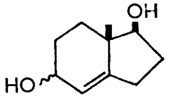
(VI)



(VII)



(VIII)



(IX)

Attention was next turned to catalytic reduction of *O*-derivatives of the ketol (II) as it seemed possible that a bulky substituent might cause the compound to be adsorbed [7] from the α-face. The ketol benzoate was readily prepared but on hydrogenation and subsequent removal of the benzoyl group afforded the *cis*-compound (IV). The triphenylmethyl derivative was also made but could not be hydrogenated except under conditions which removed the trityl group.

Lithium aluminium hydride reduced the diketone (I) to two enediols (IX) (m. p. 101—103°, 60%; m. p. 145°, 16%) which were separated by chromatography. As the mixture gave, in high yield, the ketol (II), on treatment with manganese dioxide, these compounds were epimeric at $C_{(5)}$. Catalytic reduction of the compound of m. p. 101° under neutral conditions afforded the *cis*-monoalcohol (VI) and a saturated diol. The ring junction in

[2] Fieser and Fieser, " Steroids," Reinhold Publ. Corp., New York, 1959.

[3] Prelog and Acklin, *Helv. Chim. Acta*, 1958, **41**, 1428.

[4] Cf. Barton and Robinson, *J.*, 1954, 3045; Birch, Smith, and Thornton, *J.*, 1957, 1339.

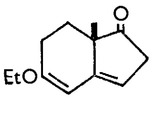
[5] Johnson, *J. Amer. Chem. Soc.*, 1944, **66**, 215.

[6] Woodward, Sondheimer, Taub, Heusler, and McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223.

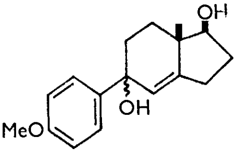
[7] Linstead, Doering, Davis, Levine, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1958.

the latter was proved to be *cis* by oxidation to the *cis*-dione (VIII). In order to minimise hydrogenolysis, the enediol of m. p. 145° was hydrogenated with only a trace of catalyst present. One mol. of gas was taken up and a saturated diol isomeric with that above was obtained. This second diol could be obtained directly from the ketol (II) by hydrogenation with platinum under acid conditions.* By oxidation this compound also was shown to have a *cis*-ring junction. It is difficult to assign complete configurations to these compounds, because, as *cis*-ring junctions are involved, each diol can adopt two conformations. However, we believe[8] the compound of m. p. 101° to be the 5β-epimer (angular methyl assigned a β-symbol). The separation of the enediols (IX) on alumina was often accompanied by appearance of a carbonyl band in the infrared absorption of the eluates; this was particularly marked with alumina of high activity and can only be rationalised by a hydrogen-transfer † [(IX) to (IV)].

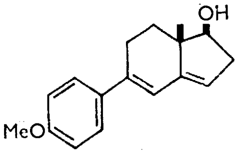
It was by now clear that reduction of the 4,9-double bond always gave a *cis*-junction. We next decided to move this bond into the five-membered ring as there is ample evidence in the steroids themselves that a 14,15-double bond will accept hydrogen from the α-side.[2] The diketone (I) with triethyl orthoformate and hydrogen chloride under anhydrous conditions gave the enol ether (X): its ultraviolet absorption [$\lambda_{max.}$ (in cyclohexane) 247 mμ; ε 14,500] was consistent with a heteroannular arrangement of double bonds. Hydrogenation proceeded quantitatively with ethanol and palladium–strontium carbonate; the intermediate was hydrolysed without isolation and afforded 4,5,6,7,8,9-hexahydro-8-methyl-*cis*-indane-1,5-dione (VIII): no other compound was isolated.



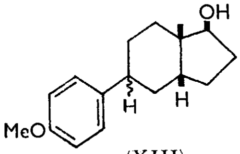
(X)



(XI)



(XII)



(XIII)

The ketol (II) with *p*-methoxyphenyl-lithium gave the allylic alcohol (XI), readily dehydrated to a diene which is formulated as (XII) on the basis of its light absorption. Catalytic hydrogenation of this compound under neutral conditions gave a tetrahydro-derivative (XIII) which could possess either a *cis*- or a *trans*-ring junction. To establish this a similar sequence of reactions was carried out on the saturated *cis*-ketol (IV). The product was identical with that above, thus establishing a *cis*-ring junction in the compound (XIII). As a *trans*-compound had not been formed, further modification to a testosterone analogue was not carried out.

In a catalytic hydrogenation the four main variables are the compound, the medium, the catalyst, and the temperature. Experience shows that slight variations in the first two often profoundly influence the stereochemical nature of the product. It is difficult to see why the *trans*-junction was not established in some of the above reactions.

EXPERIMENTAL

All the 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.

5,6,7,8-*Tetrahydro*-1β-*hydroxy*-8-*methylindan*-5-*one* (II).—A solution of sodium borohydride

---

* The preferential formation of axial hydroxyl groups in acid solution (Barton, *J.*, 1953, 1027) cannot be used to assign a configuration to this diol because of the non-rigid *cis*-ring junction.

† Such reactions are usually brought about with acids.[9]

[8] Boyce, Ph.D. Thesis, Exeter, 1959.

[9] Cf. Dreiding and Hartman, *J. Amer. Chem. Soc.*, 1956, **78**, 1216; Djerassi, Smith, Lippman, Figdor, and Herran, *ibid.*, 1955, **77**, 4801; Mosettig and Nes, *J. Org. Chem.*, 1955, **20**, 884; Hearne, Tamele, and Converse, *Ind. Eng. Chem.*, 1941, **33**, 805.

(1·02 g.) (recrystallised from diethylene glycol dimethyl ether) in propan-2-ol (100 ml.) and ethanol (100 ml.) was added during 45 min. to a stirred solution of 5,6,7,8-tetrahydro-8-methylindane-1,5-dione (I) (16·4 g.) in ethanol (50 ml.) at 0°. The mixture was stirred for a further 15 min., and then allowed to reach room temperature during an additional 20 min. Acetic acid (2 ml.) was added, the dark brown solution becoming orange. Evaporation under reduced pressure gave a gum which was dissolved in chloroform and washed with water. The dried ($MgSO_4$) organic layer was distilled; the *ketol* (13·55 g., 82%) had b. p. 140—144°/0·05 mm., n_D^{17} 1·5310, $\lambda_{max.}$ 242 mμ (ε 11,500), $\nu_{max.}$ (liquid film) 3420, 1640, 1440, 1420, 1354, 1322, 1270, 1218, 1140, 1086, 1076, 1035, 1026, 1005, 956, and 870 cm.$^{-1}$ (Found: C, 71·4; H, 8·4. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%). Chromatography on alumina and elution with ether yielded identical fractions. The 2,4-*dinitrophenylhydrazone* crystallised from ethanol as scarlet plates, m. p. 149—149·5° (Found: C, 56·2; H, 5·5; N, 15·5. $C_{16}H_{18}N_4O_5$ requires C, 55·5; H, 5·2; N, 16·1%). The semicarbazone had m. p. 180·5—181·5° (from ethanol) and the 3,5-dinitrobenzoate crystallised from ethanol as needles, m. p. 90—91°.

4,5,6,7-cis-8,9-*Hexahydro*-8-*methylindane*-1,5-*dione* (VIII).—5,6,7,8-Tetrahydro-8-methylindane-1,5-dione (I) (2·0 g.) in ethanol (50 ml.) was hydrogenated at room temperature and pressure over 2% palladised calcium carbonate (1 g.). Uptake ceased after 10 min. at 1 mol. Removal of catalyst and solvent, and filtration of the oily residue in ether through alumina, gave a solid (1·4 g.), m. p. 66—67°. Recrystallisation from 2 : 1 ether–light petroleum furnished the pure cis-*dione*, m. p. 71·5—72·5° (Found: C, 72·2; H, 8·6. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%), $\nu_{max.}$ (liquid film) 1737, 1720, 1448, 1420, 1370, 1338, 1144, 1090, and 1050 cm.$^{-1}$. The *bis*-2,4,-*dinitrophenylhydrazone* crystallised from tetrahydrofuran–ethanol as an orange powder, m. p. 165° (Found: C, 50·8; H, 4·5. $C_{22}H_{22}N_8O_8$ requires C, 50·2; H, 4·2%). The semicarbazone was highly insoluble.

4,5,6,7-cis-8,9-*Hexahydro*-1β-*hydroxy*-8-*methylindan*-5-*one* (IV).—(*a*) 5,6,7,8-Tetrahydro-1β-hydroxy-8-methylindane-5-one (II) (2·35 g.) in ethanol (20 ml.) was shaken with 2% palladium–strontium carbonate (500 mg.) in hydrogen. Reduction (1 mol.) ceased after 15 min. Removal of catalyst and solvent left a waxy solid, m. p. 80—83°. Remarkable changes occurred on attempted crystallisation and chromatography; the substance had a tendency to form a solid foam, the material of which was quite hard but was not obviously crystalline.

The 2,4-*dinitrophenylhydrazone* had sharp but variable m. p.s, *e.g.*, 134°, 136—137°, and 155—156° (Found: C, 55·5; H, 6·0; N, 15·8. $C_{16}H_{20}N_4O_5$ requires C, 55·2; H, 5·8; N, 16·1%).

(*b*) A solution of 5,6,7,8-tetrahydro-1β-hydroxy-8-methylindane-5-one (II) (3·0 g.) in dry ether (50 ml.) was added during 10 min. to a stirred solution of lithium (300 mg.) in distilled liquid ammonia (150 ml.). The mixture was stirred for 10 min. more, then dry ammonium chloride was added to discharge the blue colour. Evaporation of the ammonia left a gum which was dissolved in ether; the ethereal solution was washed with water, then dried ($MgSO_4$) and concentrated. The colourless solid (2·7 g.) which remained could not be crystallised. The 2,4-dinitrophenylhydrazone after one recrystallisation had m. p. 155—156°; subsequently after six recrystallisations it had m. p. 134° and gave no depression with the 2,4-dinitrophenylhydrazone above. The intermediate m. p.s were sharp but variable. The infrared spectra of the two samples in chloroform solution were identical.

The above ketol (550 mg.) in acetone (30 ml.) was treated dropwise with 8N-chromic acid, and the product worked up in the usual way. Crystallisation from 2 : 1 ether–light petroleum deposited 4,5,6,7-*cis*-8,9-hexahydro-8-methylindane-1,5-dione (410 mg.), m. p. and mixed m. p. 71—72°.

4,5,6,7-cis-8,9-*Hexahydro*-8-*methylindan*-1-*one* (VII).—4,5,6,7-*cis*-8,9-Hexahydro-1β-hydroxy-8-methylindane-5-one (IV), ethylene glycol (75 ml.), and 100% hydrazine hydrate (15 ml.) were heated at 90—100° for 1 hr. Potassium hydroxide (2·5 g.) was added, the temperature raised to 210°, and heating continued for 5 hr. with slow distillation. The cooled mixture and distillate were poured into water and extracted with ether. The ethereal solution was washed with water, then dried ($MgSO_4$) and concentrated. The residue, which had a strong smell of camphor, was distilled to give 4,5,6,7-*cis*-8,9-hexahydro-8-methylindan-1β-ol (VI) (2·2 g.), b. p. 120°/14 mm., which immediately solidified and had m. p. 51·5—54°. The infrared spectrum (solid film) had main bands at 3420, 1452, 1065, 1028, 1000, 950, 878, and 860 cm.$^{-1}$.

The product was treated in acetone (30 ml.) dropwise with 8N-chromic acid in the usual way. 4,5,6,7-*cis*-8,9-Hexahydro-8-methylindane-1-one (VII), b. p. 96—100°/12 mm., n_D^{17} 1·4780, was obtained. Johnson[5] gives b. p. 106°/20 mm., m. p. 34·5—36°.

The 2,4-dinitrophenylhydrazone and the semicarbazone were identical with specimens kindly provided by Professor W. S. Johnson.

1β-*Benzoyloxy*-4,5,6,7-cis-8,9-*hexahydro*-8-*methylindan*-5-*one*.—5,6,7,8-Tetrahydro-1β-hydroxy-8-methylindane-5-one (II) (2·75 g.) was dissolved in pyridine (5 ml.) and treated with benzoyl chloride (5 ml.). The following morning the mixture was poured on ice and extracted with ether. The ethereal solution was washed with sodium hydrogen carbonate solution and water and dried ($MgSO_4$). Removal of solvent and distillation of the residue gave the *benzoate*, b. p. 156°/0·05 mm., n_D^{20} 1·5610 (Found: C, 74·9; H, 6·9. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%), $\nu_{max.}$ (liquid film) 1720, 1690, 1440, 1270, 1106, 1072, 1024, 1000, 950, 890, and 700 cm.$^{-1}$.

The benzoate (1·65 g.) in ethanol (20 ml.) was hydrogenated over 2% palladium–strontium carbonate (200 mg.) at room temperature and pressure. After 90 min., when the theoretical uptake for 1 mol. had been reached, absorption ceased. The mixture was filtered, treated with a solution of potassium hydroxide (1 g.) in water (10 ml.), and refluxed for 1 hr. It was then cooled, poured into water, and extracted with ether. The ethereal solution was washed with dilute hydrochloric acid, sodium hydrogen carbonate solution, and water and dried ($MgSO_4$). Distillation gave 4,5,6,7-*cis*-8,9-hexahydro-1β-hydroxy-8-methylindan-5-one (IV), b. p. 110—113°/0·05 mm.; oxidation in the usual manner gave, after chromatography on neutral alumina (30 g., Grade II) and elution with 2 : 1 ether–light petroleum, the corresponding dione, m. p. and mixed m. p. 71·5—72·5°.

5,6,7,8-*Tetrahydro*-8-*methyl*-1β-*trityloxyindan*-5-*on*.—A solution of the ketol (II) (1·35 g.) in pyridine (25 ml.) was refluxed for 16 hr. with freshly recrystallised chlorotriphenylmethane (4·6 g.). The dark solution was concentrated under reduced pressure, and the residue adsorbed from benzene (15 ml.) on neutral alumina (40 g.). Elution with 4 : 1 light petroleum–ether removed triphenylmethanol. Further elution with ether afforded the *trityl derivative* (370 mg.), m. p. 220° (from acetone–water) (Found: C, 85·0; H, 7·3. $C_{29}H_{28}O_2$ requires C, 85·3; H, 6·9%). Hydrogenation of this trityl derivative under neutral conditions could not be achieved.

Reduction of 5,6,7,8-*Tetrahydro*-8-*methylindane*-1,5-*dione by Lithium Aluminium Hydride*.—A solution of the dione (4·0 g.) in ether (75 ml.) was added during 30 min. to a gently refluxing solution of lithium aluminium hydride (1·9 g.) in ether (75 ml.) and refluxing continued for 1 hr. The excess of reagent was decomposed with ethyl acetate, dilute sulphuric acid and chloroform were added, and the organic layer was washed well with water and then dried ($MgSO_4$). After removal of solvents at reduced pressure a gum (3·68 g.) remained. This diol mixture (3·25 g.) (no carbonyl absorption in the infrared) was adsorbed from the minimum quantity of chloroform on to neutral alumina (80 g.; Grade IV) and diluted with chloroform–dry ether (0—100% of ether), 40 ml. fractions being collected; numbers 1—7 gave oils (100 mg.); 8—21, gums (1·97 g.); 22—34, oils (390 mg.). Further elution with ether–ethanol (40 : 1) gave fractions 35—41, gums (380 mg.). Fractions 8—21 were combined and rechromatographed on alumina (40 g.; Grade IV). Elution with ether gave a gum which, after trituration with light petroleum and crystallisation from ethyl acetate, afforded a 5,6,7,8-*tetrahydro*-8-*methylindane*-1β,5ξ-*diol* (IX), m. p. 101—103° (Found: C, 71·9, 72·0; H, 9·4, 9·1. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%), $\nu_{max.}$ (Nujol mull) 3340, 1375, 1340, 1325, 1095, 1084, 1064, 1040, 1028, 1007, 980, 966, and 865 cm.$^{-1}$.

Fractions 22—34 were uncrystallisable.

Fractions 35—41 were combined and triturated with ethyl acetate; recrystallisation from the same solvent furnished the epimeric *diol* (IX), m. p. 142—143° (Found: C, 71·3; H, 9·6%), $\nu_{max.}$ (Nujol mull) 3340, 1380, 1338, 1090, 1080, 1040, 1024, 1007, 984, 948, 912, and 864 cm.$^{-1}$.

The crude diol mixture (420 mg.) in purified chloroform (50 ml.) was stirred for 2 days with precipitated manganese dioxide. Working up in the usual way gave an oil which furnished a scarlet 2,4-dinitrophenylhydrazone (520 mg.) identical with that of 5,6,7,8-tetrahydro-1β-hydroxy-8-methylindan-5-one (II).

Catalytic Reduction of the Diols (IX).—(*a*) The diol of m. p. 101—103° (720 mg.) was hydrogenated over 2% palladium–calcium carbonate (500 mg.) in ethanol (50 ml.). After 2 hr. (1·58 mol. of hydrogen absorbed), catalyst and solvent were removed and the resultant oil was treated with hot light petroleum. The solid left (210 mg.) crystallised from ether and gave a 4,5,6,7-cis-8,9-*hexahydro*-8-*methylindane*-1β,5ξ-*diol* as colourless prisms, m. p. 133—134° (Found: C, 70·8; H, 10·4. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·7%), $\nu_{max.}$ (in Nujol) 3250, 1294, 1068, 1044, 1016, 992, and 968 cm.$^{-1}$.

Evaporation of the petroleum solution gave a camphoraceous oil which on distillation furnished 4,5,6,7-*cis*-8,9-hexahydro-8-methylindan-1β-ol (470 mg.), b. p. 120°/14 mm., n_D^{17}

1·5151, which solidified. Oxidation in the usual manner furnished the *cis*-ketone, characterised as its 2,4-dinitrophenylhydrazone and semicarbazone.

The saturated diol, m. p. 133—134° (95 mg.), was treated in acetone dropwise with 8N-chromic acid, and the product worked up in the usual way. The *cis*-dione (VIII), m. p. and mixed m. p. 71°, was obtained.

(*b*) The diol (IX), m. p. 142—143° (105 mg.), in ethanol (20 ml.) was hydrogenated over 2% palladised–strontium carbonate (20 mg.). Reduction was stopped after 35 min. at 1 molar uptake of hydrogen. Crystallisation of the product from ether afforded a 4,5,6,7-cis-8,9-*hexahydro*-8-*methylindane*-1β,5ξ-*diol*, m. p. 161° (Found: C, 69·7; H, 10·4. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·7%), $\nu_{max.}$ (Nujol mull) 3500, 1162, 1076, 1056, 1028, 1012, 960, and 944 cm.$^{-1}$.

Oxidation of the product in the usual way gave the *cis*-dione, m. p. and mixed m. p. 71—72°.

The ketol (770 mg.) in glacial acetic acid (50 ml.) was hydrogenated over pre-reduced Adams catalyst (50 mg.). After 15 min. 1 mol. had been absorbed and after 2 hr., when uptake had reached 2 mol., absorption ceased. On removal of catalyst and solvent and trituration of the residue with ether–light petroleum, a solid (510 mg.), m. p. 154—157°, separated. Recrystallisation from ether afforded the 4,5,6,7-*cis*-8,9-hexahydro-8-methylindane-1β,5ξ-diol, m. p. 161°, identical with the compound above.

5-*Ethoxy*-2,6,7,8-*tetrahydro*-8-*methylinden*-1-*one* (X).—A solution of 5,6,7,8-tetrahydro-8-methylindane-1,5-dione (I) (5 g.) in dry benzene (50 ml.) was treated with triethyl orthoformate (4·7 g.) and 5% ethanolic hydrogen chloride (1 ml.) and refluxed for 3 hr. After being cooled, the mixture was diluted with ether and then washed with 5% sodium hydroxide solution (20 ml.). After removal of solvent, distillation afforded the *enol ether* (4·75 g.), b. p. 84—88°/0·02 mm., m. p. 51—53° (from light petroleum), $\lambda_{max.}$ (in cyclohexane) 247—248 mμ (ε 14,500). It decomposed on storage overnight.

The enol ether (1·55 g.) in ethanol (20 ml.) was treated with hydrogen and 2% palladium-calcium carbonate (500 mg.); 1 mol. of hydrogen was absorbed in 2 hr. Solvent and catalyst were removed and the residue was dissolved in 95% ethanol (50 ml.) and treated with sulphuric acid (1 ml.). After being refluxed for 1 hr., the solution was cooled, poured into brine, and extracted with ether. The extract was washed with water and then dried ($MgSO_4$) and concentrated. The residual oil crystallised from 2 : 1 ether–light petroleum to give the *cis*-dione (VIII), m. p. and mixed m. p. 71—72°.

Steroid Analogues lacking Ring B.—5,6,7,8-*Tetrahydro*-5-p-*methoxyphenyl*-8-*methylindane*-1β,5ξ-*diol* (XI).—A solution of 5,6,7,8-tetrahydro-1β-hydroxy-8-methylindan-5-one (II) (4·7 g.) in ether (150 ml.) was added to a solution of *p*-methoxyphenyl-lithium [from butyl bromide (17·1 g.)] in ether (200 ml.) at −30° under nitrogen. Sufficient tetrahydrofuran was added to dissolve the precipitate, and the clear solution was then stoppered and stored overnight at 10°. After addition of water the mixture was extracted with ether, dried ($MgSO_4$), and concentrated (100°/0·07 mm.). The benzene-soluble part of the product on crystallisation gave the *compound* (XI) (3·8 g.), m. p. 142—144°, as plates (Found: C, 74·2; H, 7·7. $C_{17}H_{22}O_3$ requires C, 74·4; H, 8·1%). The compound became pink when stored for several days. The benzene-insoluble portion of the residue when crystallised from ethanol gave colourless prisms (0·67 g.), m. p. 159—160°, that were not further investigated.

2,6,7,8-*Tetrahydro*-5-p-*methoxyphenyl*-8-*methylinden*-1β-*ol* (XII).—A portion of the freshly crystallised diol (1·9 g.) was refluxed in benzene (50 ml.) with a crystal of iodine under a Dean–Stark water separator. When water had ceased to separate, the cooled solution was washed, dried, and concentrated. Adsorption on neutral alumina (60 g.; Grade II) and elution with light petroleum–benzene (2 : 1) gave colourless crystals, m. p. 89—90°, of the diene. The substance rapidly darkened and for the next step was used directly. It had a broad absorption maximum at 290—294 mμ (ε 25,000) with a slight inflexion at 237 mμ. The infrared spectrum (Nujol mull) had bands at 1600, 1512, 1460, 1372, 1282, 1258, 1232, 1174, 1152, 1120, 1110, 1072, 1032, 970, 878, and 830 cm.$^{-1}$.

4,5,6,7-cis-8,9-*Hexahydro*-5-p-*methoxyphenyl*-8-*methylindan*-1β-*ol* (XIII).—(*a*) The freshly crystallised diene (420 mg.) in ethanol (15 ml.) was hydrogenated over 2% palladium–strontium carbonate (20 mg.). After 20 min. 1 mol. had been absorbed, and after a further 45 min. uptake ceased at 1·85 mol. Removal of catalyst and solvent gave a gum which was adsorbed from ether (10 ml.) on alumina (20 g.; Grade II). Elution with ether gave a series of homogeneous fractions. Crystallisation from ether–light petroleum furnished the cis-*hexahydroindanol* (305 mg.), m. p. 95—97° (Found: C, 78·4; H, 9·3. $C_{17}H_{24}O_2$ requires C, 77·4; H, 9·3%).

(*b*) A solution of 4,5,6,7-*cis*-8,9-hexahydro-1β-hydroxy-8-methylindan-5-one (IV) (2·3 g.) in ether (100 ml.) was added dropwise to a stirred solution of *p*-methoxyphenyl-lithium [from butyl bromide (8·25 g.)] at −15°. Sufficient tetrahydrofuran was added to dissolve the precipitate, and stirring was continued for 30 min. The clear solution was warmed to 0° and after a further 10 min. was poured on ice. Working up in the usual way and dehydration of the product as described above gave 6,7-cis-8,9-*tetrahydro*-5-p-*methoxyphenyl*-8-*methylindan*-1β-*ol* (3·1 g.), m. p. 81—83° (from ether–light petroleum) (Found: C, 78·3; H, 8·4. $C_{17}H_{22}O_2$ requires C, 79·0; H, 8·6%). The compound (1 g.) in ethanol (20 ml.) was hydrogenated over 2% palladium–strontium carbonate (200 mg.). Uptake ceased at 1 mol. after 22 min. Removal of catalyst and solvent, and crystallisation of the residue from ether–light petroleum, furnished the *cis*-hexahydrindanol, m. p. 95—97°, identical with the compound above.

We thank the Chemical Society for a grant from the Research Fund, the Council of this University and the Ministry of Education for a maintenance grant (to C. B. C. B.), and Imperial Chemical Industries Limited for financial aid.

THE WASHINGTON SINGER LABORATORIES,
THE UNIVERSITY, EXETER.

[*Received, April 6th,* 1960.]