118. *Fused Carbon Rings. Part XV. Synthesis of Derivatives of 8-Methylhydrindane and of Perhydroanthracene from Substances containing a* n-*Butenyl Side Chain. Dehydrogenation of 8-Methylhydrindane.*

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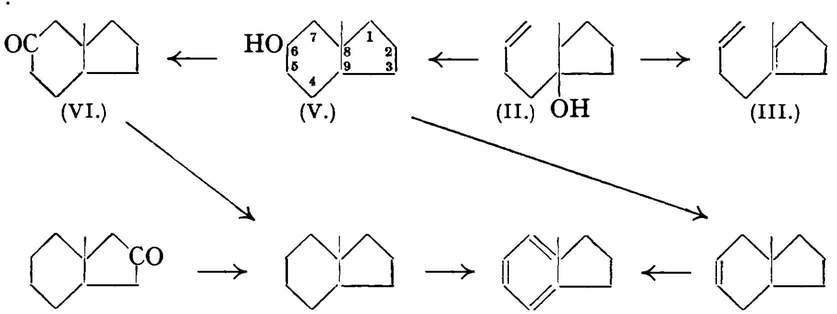
The paper is mainly concerned with an extension of a synthetic method for the fusion of *cyclo*hexane rings on to alicyclic systems. The method is to introduce a *n*-Δ^{γ}-butenyl side chain by the Grignard reaction and to cyclise the tertiary alcohol so obtained by acetic and sulphuric acids or by phosphoric acid. In this way 8-methyl-6-hydrindanol and 2-perhydroanthrol have been made from 2-methyl*cyclo*pentanone and *trans*-β-decalone respectively. The structure of 8-methyl-6-hydrindanol has been established (i) by degradation to 1-methyl*cyclo*pentane-1-carboxylic-2-acetic acid, which has been independently synthesised, together with various isomeric acids; (ii) by conversion into the known 8-methylhydrindane. The configurations of the various compounds are discussed.

Catalytic dehydrogenation of 8-methylhydrindane under suitable conditions yields hydrindene, there being no ring enlargement or migration of the methyl group. The result is of interest in connection with the dehydrogenation of sterols and similar compounds.

IN previous papers of this series (Parts VII, VIII, XIII, and XIV) we have described the preparation of 8-methylhydrindane (I) and of various of its derivatives, substituted in the five-membered ring, which were obtained by the degradation of angular-methylated derivatives of decalin. Other compounds containing the same carbon skeleton have been described by Clemo and Dickenson (J., 1935, 735), Chuang, Ma, and Tien (*Ber.*, 1935, **68**, 1946), and du Feu, McQuillin, and Robinson (J., 1937, 53). In view of the special interest attaching to this structure, which constitutes half the aetiocholane molecule, we have now studied the direct synthesis of derivatives of 8-methylhydrindane, substituted in the six-membered ring, by the "butenyl" method (Hibbit and Linstead, J., 1936, 470; cf. J., 1936, 476; 1937, 1136, 1140).

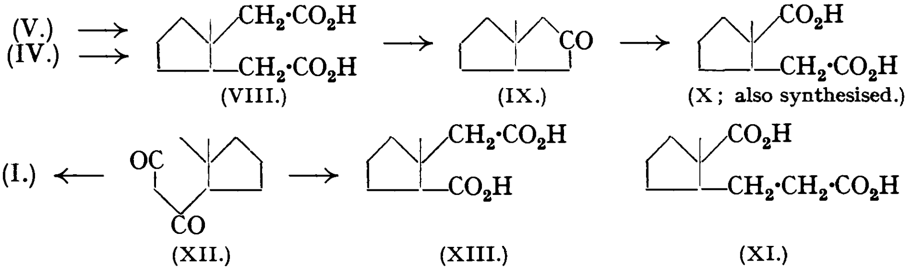
When 2-*methyl*-1-Δ^{γ}-*butenyl*cyclo*pentanol* (II) is dehydrated by oxalic acid, it yields the corresponding *diolefin* (III), but the action of a mixture of phosphoric acid and anhydride yields the dicyclic *mono-olefin* (IV). This is also formed by similar treatment of the diene (III). If the alcohol is treated with a mixture of sulphuric acid, acetic acid, and acetic anhydride (Linstead, Millidge, and Walpole, J., 1937, 1140), the main product is the acetate of 8-*methyl*-6-*hydrindanol* (V), and hydrolysis yields the dicyclic alcohol as a crystalline solid. These reactions parallel those observed with the corresponding derivatives of *cyclo*hexane. Oxidation of the alcohol (V) with chromic acid yields the corresponding 8-methyl-6-hydrindanone (VI), which is reduced by Clemmensen's method to 8-methylhydrindane (I), identical with that obtained by the reduction of 8-methyl-2-hydrindanone (VII) (Linstead, Millidge and Walpole, *loc. cit.*). As the hydrocarbon is a crystalline solid of m. p. 12°, the identity of the products has been established with certainty.



This evidence proves the structure of the carbon framework of the alcohol (V) and also establishes that the configuration is identical with that (probably *cis*) of 8-methyl-2-hydrindanone (VII) and the related compounds mentioned in earlier papers. It does not establish the position of the hydroxyl group. This is placed in position 6 by analogy with the syntheses of *cis*-β-decalol and of 9-methyl-2-decalol, and from the following evidence.

Oxidation of the alcohol (V) with nitric acid yields a dibasic acid $C_{10}H_{16}O_4$, m. p. 103°, and the same acid is formed by permanganate oxidation of the olefin (IV). This compound must be a 1-methyl*cyclo*pentane derivative, either the 1-carboxylic-2-β-propionic acid, the 1 : 2-diacetic acid (VIII), or the 1-β-propionic-2-carboxylic acid. Direct comparison shows that it is not identical with 1-methyl*cyclo*pentane-2 : 2-diacetic acid, which would be formed by the oxidation of a *spiro*-ketone. When heated with baryta, it yields a saturated dicyclic ketone, $C_9H_{14}O$, which must be a 7-methyl*bicyclo*[0 : 3 : 3]octanone with the keto-group in position 1, 2, or 3. Oxidation of the ketone gives an acid, $C_9H_{14}O_4$, m. p. 110°. This has been identified as *1-methyl*cyclo*pentane-1-carboxylic-2-acetic acid* (X) by an independent synthesis, which is described later. This proves that the 7-methyl*bicyclo*-octanone is the 1- or 2- and not the 3-ketone, and hence that the parent acid, $C_{10}H_{16}O_4$, is either the *diacetic acid* (VIII) or the 1-carboxylic-2-β-propionic acid.

It is difficult to foresee the position of oxidation of an alcohol of structure (V). A. H. Cook and Linstead found that 5-hydrindanol, which contains the same ring system, was oxidised to a carboxy-propionic acid (J., 1934, 946; cf. Hückel, Goth, and Demmler, *Ber.*, 1934, **67**, 2102). On the other hand, 9-methyl-2-decalol, which contains a similar orientation of hydroxylic and angular methyl groups, is oxidised to a diacetic acid (Linstead, Millidge, and Walpole, *loc. cit.*). It seems probable that, in the present case, the oxidation product is the diacetic acid (VIII), and hence the ketone is the 2-isomeride (IX), for the following reasons : (i) The C_{10}-acid is esterified with comparative ease to a neutral ester, whereas the 1-carboxyl group of the alternative structure (XI) would be expected to resist esterification. (ii) The C_9-ketone readily yields a semicarbazone in the cold. This parallels the behaviour of 8-methyl-2-hydrindanone, but the 1-ketone is less reactive (Linstead, Millidge, and Walpole, *loc. cit.*) and exhibits the lowered ketonic reactivity observed by Cornubert among many ketones containing two α-substituents (compare also 9-methyl-1-, -2-, and -3-decalones). This evidence is not, of course, conclusive.



To establish the identity of the final oxidation product (the acid $C_9H_{14}O_4$, m. p. 110°), we have synthesised the carboxylic-acetic acid (X) in both *cis*- and *trans*-forms. The two forms of the isomeric 1-acetic-2-carboxylic acid (XIII) had already been made by Chuang and his collaborators (*loc. cit.*) by the oxidation of 4 : 6-diketo-8-methylhydrindane (XII), first prepared by Clemo and Dickenson (*loc. cit.*). Chuang noted that the diketone was oxidised to an acid, m. p. 166°, which formed a stable anhydride, but was itself unstable, being converted by hydrochloric acid at 200° into a stereoisomeride of m. p. 101°. The second acid gave the anhydride of the acid of m. p. 166°. On these grounds Chuang assigned the *cis*-configuration to the 166° acid. Clemo and Dickenson, however, gave the *trans*-configuration to the methylhydrindane obtained by the reduction of the diketone (XII). We have confirmed the results of the Chinese workers (except that the oxidation product of the diketone melted at 169°). The 8-methylhydrindane obtained by reduction of the diketone, although not quite homogeneous, was essentially the same as that obtained by the reduction of the 8-methylhydrindanones (VI) and (VIII). We consider the *cis*-

configuration to be very probable for the diketone (XII) from Hückel's observations of the relative stabilities of *cis*- and *trans*-α-ketohydrindanes, and this to be confirmed by Chuang's evidence, which parallels the observations of A. H. Cook and Linstead (J., 1934, 956) on the corresponding unmethylated acids, the configurations of which are known with certainty. Moreover, the formation of essentially the same hydrocarbon by reduction establishes the same configuration for the diketone (XII) and the monoketones (VI and VII). The cumulative evidence that this common configuration is *cis* is now very strong.

The pair of new acids (X) was synthesised from 2-methyl*cyclo*pentanone-2-carboxylic ester. This condensed with cyanoacetic ester in the presence of piperidine, with extreme reluctance under ordinary pressure, but more readily under 4000 atmospheres (compare Newitt, Linstead, Sapiro, and Boorman, J., 1937, 879). The unsaturated *cyano-ester* so obtained, after reduction and hydrolysis, yielded one form (probably *trans*) of the acid (X), m. p. 139°. Condensation of the keto-ester with ethyl bromoacetate, followed by dehydration, catalytic reduction, and hydrolysis, yielded an isomeric acid, m. p. 110°. This was identical with that obtained by the oxidation of 7-methyl*bicyclo*octanone (IX). Barrett, A. H. Cook, and Linstead (J., 1935, 1065) obtained a form of the acid (X), m. p. 126°, by the low-pressure cyanoacetic ester route. Repetition of this showed that the product was a mixture of stereoisomerides, mainly the 139° form. As in the *cyclo*hexane series (Linstead and Millidge J., 1936, 478), the Reformatsky reaction leads to the presumed *cis*-configuration, the cyanoacetic ester route to a mixture, mainly *trans*.

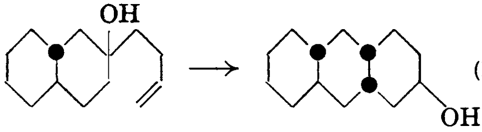
Dehydrogenation of Hydrindane, 8-Methylhydrindane, and 8-Methylhexahydroindene.—The dehydrogenation of 8-methylhydrindane is of obvious importance as a model for the behaviour of sterols and allied compounds. Clemo and Dickenson (*loc. cit.*) observed that the hydrocarbon was completely unaffected by dehydrogenating agents. We examined the action of the platinum and palladium catalysts used by Linstead, Millidge, Thomas, and Walpole (J., 1937, 1143) on stereochemically pure hydrocarbons made either by reducing regenerated ketones or (in the case of the olefin, IV) by dehydrating the solid alcohol (V). *trans*-Hydrindane was not dehydrogenated in the liquid phase at the boiling point over any catalyst, but in the vapour phase at 330° over platinised asbestos or palladised charcoal smoothly yielded indane (hydrindene, XIV). This agrees with Zelinsky and Titz's dehydrogenation of hydrindane (mainly *cis*, from the method of preparation) over platinised charcoal (*Ber.*, 1929, **62**, 2871). *cis*-8-Methylhexahydroindene (IV) was practically unaffected over platinised asbestos at 330°, but over palladised charcoal gave indane in good yield. *cis*-8-Methylhydrindane (I) behaved in exactly the same manner. The indane was in each case identified as the 5-sulphonic acid. No indene or naphthalene was formed in any experiment, and no methylindane could be detected, although the presence of a small amount cannot be excluded.

The general conclusions are: (1) The hydrindane system is more resistant towards catalytic dehydrogenation than the decalin. (2) Only the six-membered ring is dehydrogenated. (3) Under our conditions, over the most active catalyst, the angular methyl group is eliminated: there is no migration or ring enlargement: the less vigorous platinum-black catalyst is without influence. This contrasts with the behaviour of the angular group of 9-methyldecalin and octalin, which tends to migrate to the 1-position, particularly over the milder catalyst.

The absence of migration of the angular group of 8-methylhydrindane falls into line with the experiments of J. W. Cook and Girard (*Nature*, 1934, **133**, 377), Cohen, J. W. Cook, Hewett, and Girard (J., 1934, 653), and Peak and Robinson (J., 1937, 1581) on more complex compounds, and supports the general belief that the appearance of a methyl group in the five-membered ring of Diels' hydrocarbon (3′-methyl*cyclo*pentenophenanthrene) is bound up with the elimination of the long side chain.

Synthesis of 2-Perhydroanthrol.—We have also applied the butenyl method to the synthesis of a tricyclic compound. trans-2-Δ^{γ}-n-*Butenyl-2-decalol* (XV) was converted into the acetate of 2-perhydroanthrol and thence into the crystalline alcohol (XVI). The ring structure is shown by the fact that dehydration, followed by dehydrogenation, gave a good yield of anthracene. From the method of synthesis and by analogy with the formation of *cis*-β-decalol from *cyclo*hexanone, the product is a *trans-cis*-compound with the configuration shown in (XVI) (for this mode of representation, see *Chem. and Ind.*, 1937, **56**, 511).

(XV.)



(XVI.)

The formation of a hydroanthracene rather than a hydrophenanthrene derivative in this reaction provides another example of the reactivity of the 3-position in 2-decalones and similar compounds. J. W. Cook and Lawrence (J., 1937, 817), in their recent comments on this, have pointed out that both *cis*- and *trans*-compounds show this property in contrast to the sterols, where the 4-position of *cis*-3-ketones is the reactive centre in brominations and oxidations. In this respect *cis*-angular-methylated β-decalones resemble *cis*-β-decalone and not *cis*-sterol compounds such as coprostanone. Thus it has been shown (Linstead, Millidge, and Walpole, *loc. cit.*) that (*cis*-) 9-methyl-2- and -3-decalones are both oxidised at the 2—3 bond to yield 1-methyl*cyclo*hexane-1 : 2-diacetic acid in contrast to the formation of lithobilianic acid from coprostanone.

EXPERIMENTAL.

8-*Methylhydrindane Group*.—Ethyl *cyclo*pentanone-2-carboxylate (Linstead and Meade, J., 1934, 935) was converted into the sodio-compound by "molecular" sodium in light petroleum and methylated with methyl iodide, unchanged material being removed with 10% alkali solution. The methylated ester (yield, 93%; b. p. 128—131°/20 mm.) gave a 65% yield of 2-methyl*cyclo*pentanone (b. p. 139—141°; semicarbazone, m. p. 182°) on hydrolysis with hydrochloric acid (1 : 1). A solution of the ketone (98 g., 1 mol.) in 200 c.c. of anhydrous ether was added in drops to the Grignard reagent prepared from 135 g. of Δ^3-butenyl bromide (Linstead and Rydon, J., 1934, 1998). The mixture was refluxed for 2 hours and left overnight, the product decomposed with ice and ammonium chloride, and 2-*methyl*-1-Δ^{γ}-*butenyl*cyclo*pentanol* (II) isolated in the usual manner, as a colourless liquid, b. p. 87—91°/10 mm.; yield, 52 g. (35%) (Found: C, 77·7; H, 11·7. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%).

10 G. of the alcohol were heated at 150° with 15 g. of anhydrous oxalic acid for 4 hours. The product was treated with water and extracted with purified light petroleum, the extract washed with alkali and water and dried, and the solvent removed. The residue after two distillations, the second over sodium, yielded 5 g. of 2-*methyl*-1-Δ^{γ}-*butenyl*cyclo*pentene* (position of the second double bond unknown, probably as in III), a pungent-smelling liquid, b. p. 168—169°, $d_{4^\circ}^{18\cdot5^\circ}$ 0·8377, $n_{\mathrm{D}}^{18\cdot5^\circ}$ 1·4665, $[R_L]_{\mathrm{D}}$ 45·06 (calc. for $|^{=}_{2}$, 45·18) (Found: C, 88·0; H, 11·45. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%). The bromine addition under the conditions of Rosenmund and Kuhnhenn was 334 and 319 g. of bromine per mole in two determinations ($2Br_2$ requires 320). 0·1264 G. of the diene in purified acetic acid over Adams's catalyst absorbed 42·8 c.c. of hydrogen at N.T.P., corresponding to 2·03 double bonds.

5 G. of the alcohol (II) were heated at 140—150° for 5 hours with 5 g. of phosphoric oxide and 25 c.c. of phosphoric acid (*d* 1·75). The product, isolated as usual, yielded a fraction, b. p. 68—74°/14 mm., which was refluxed over sodium for 30 minutes and then redistilled. 2·5 G. of 8-*methylhexahydroindene* (probably IV) were obtained, b. p. 175—176°/761 mm., $d_{4^\circ}^{16\cdot5^\circ}$ 0·8879, $n_{\mathrm{D}}^{16\cdot5^\circ}$ 1·4825, $[R_L]_{\mathrm{D}}$ 43·69 (calc., 43·51) (Found: C, 88·1; H, 11·5. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%). The olefin absorbed 168 and 173 g. of bromine per mole (Br_2 requires 160), and over Adams's catalyst took up hydrogen corresponding to 99% hydrogenation of one double bond. Similar treatment of the diene (III) gave a product, b. p. 176°, $d_{4^\circ}^{12\cdot5^\circ}$ 0·8854, $n_{\mathrm{D}}^{12\cdot5^\circ}$ 1·4835, $[R_L]_{\mathrm{D}}$ 43·90. On catalytic hydrogenation this gave a result corresponding to the presence of 1·11 double bonds. This and the physical properties indicate that the product is the cyclic monolefin (IV) contaminated with a little unchanged diene. 8-Methylhexahydroindene with very similar properties (b. p. 176°, $d_{4^\circ}^{19^\circ}$ 0·8891, $n_{\mathrm{D}}^{19^\circ}$ 1·4810, $[R_L]_{\mathrm{D}}$ 43·58) was also made by dehydrating pure solid 8-methyl-6-hydrindanol with potassium hydrogen sulphate.

23 G. of the alcohol (II) were slowly added at 0° to 150 c.c. of a reagent made from glacial acetic acid (200 c.c.), acetic anhydride (20 c.c.), and concentrated sulphuric acid (20 c.c.). After 5 days' standing, the mixture was worked up as described by Linstead, Wang, Williams, and Errington (J., 1937, 1136), and the crude acetate hydrolysed. Distillation of the neutral product of the hydrolysis yielded 1·8 g., b. p. 80—105°/18 mm. (mainly olefin), and 16 g., b. p.

106—116°/10 mm. The second fraction rapidly solidified to a camphor-like mass, which was drained on a porous tile and crystallised from purified light petroleum. 12 G. of pure cis-*8-methyl-6-hydrindanol* (V) were so obtained, m. p. 66° (Found: C, 77·7; H, 11·4. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). Extraction of the tile with ether and distillation gave 3 g. of a strong-smelling liquid isomeride (mainly an epimeride), b. p. 112—113°/11 mm.

Oxidation of 6 g. of the pure solid alcohol with 3 g. of chromic acid in 20 c.c. of glacial acetic acid in the usual manner gave 4·5 g. of a ketone, b. p. 107—108°/12 mm., m. p. about 24°. This reacted rapidly in the cold with semicarbazide acetate in aqueous methyl alcohol. The *semicarbazone* of *cis*-8-methyl-6-hydrindanone crystallised from methyl alcohol in large clusters, m. p. 210° (bath preheated to 200°) (Found: C, 63·5; H, 9·1. $C_{11}H_{19}ON_3$ requires C, 63·1; H, 9·2%). The same semicarbazone was obtained from the ketone, b. p. 109°/13 mm., made by oxidising the liquid alcohol mentioned above. In neither case could an isomeric semicarbazone be detected. Regeneration from the semicarbazone yielded *cis*-8-methyl-6-hydrindanone, b. p. 109°/12 mm., m. p. 37°. Reduction of this by Clemmensen's method, followed by purification of the product by washing with concentrated sulphuric acid and refluxing over sodium, yielded *cis*-8-methylhydrindane, b. p. 69°/19 mm., m. p. 12—13°, $d_4^{16°}$ 0·8778, $n_D^{16°}$ 1·4707, $[R_L]_D$ 43·96 (calc., 43·98). This hydrocarbon was practically identical in properties with that prepared by Linstead, Millidge, and Walpole (*loc. cit.*) and did not depress its m. p.

5 G. of 8-methyl-6-hydrindanol were added slowly with occasional cooling to 10 c.c. of concentrated nitric acid. After 2 hours the solution was heated to boiling and diluted with 20 c.c. of water. Solid separated from the cooled solution and more was obtained by evaporation in a vacuum desiccator. Yield, 3 g. of crude acid, giving, after crystallisation from water, 2·2 g. of pure cis-1-*methyl*cyclo*pentane*-1 : 2-*diacetic acid** (VIII) in clusters of transparent prisms, m. p. 103°, sparingly soluble in cold water, readily in hot (Found: C, 59·6; H, 8·1; equiv., 99·6. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·1%; equiv. 100·1). The same acid was obtained by oxidation of 8-methylhexahydroindene (IV) (6 g.) with 700 c.c. of 3% potassium permanganate solution at 0°. The product was worked up as usual, acidified, and extracted six times by hand and then continuously for 2 days. Both the hand and the constant-ether extracts yielded an oily residue, which deposited the acid (VIII), m. p. (crude) 101°, 102—103° after crystallisation. Esterification of the acid (0·3 g.) with 7 c.c. of methyl alcohol and 1 c.c. of sulphuric acid (1 hour at the b. p.) gave a neutral ester (b. p. 120—130°/3 mm.) and no appreciable amount of acid ester.

4·8 G. of the dibasic acid were heated with a crystal of baryta in a fused nitrate bath at 280—290°. Ketone distilled over at once, and was extracted from the distillate with light petroleum. The extract was washed with alkali, dried, and evaporated. *cis*-7-Methyl*bicyclo*[0 : 3 : 3]-octanone (probably the 2-ketone, IX) boiled at 80°/12 mm., melted at 26°, and readily gave a *semicarbazone* in the cold, m. p. 178° (from methyl alcohol) (Found: C, 62·1; H, 8·6. $C_{10}H_{17}ON_3$ requires C, 61·5; H, 8·8%). 2·5 G. of the ketone were slowly added to 20 c.c. of concentrated nitric acid; after 5 minutes, the mixture was diluted with 15 c.c. of water, boiled for 15 minutes, and left over alkali in a vacuum desiccator. cis-1-*Methyl*cyclo*pentane*-1-*carboxylic*-2-*acetic acid* (X) then separated, m. p. 100—104° (crude), 110° after two crystallisations from water (Found: C, 57·9; H, 7·7. $C_9H_{14}O_4$ requires C, 58·1; H, 7·5%). It formed prisms, sparingly soluble in cold water, readily in hot.

Synthesis of Various Methyl cyclo*Pentanecarboxylicacetic Acids.*—(*a*) Dr. R. H. Sapiro of this College kindly carried out for us the condensation between equimolecular quantities of ethyl 2-methyl*cyclo*pentanone-2-carboxylate and ethyl cyanoacetate in the presence of piperidine at 65° under 5000 atmospheres. The reaction yielded 20% of *ethyl 2-methyl*cyclo*pentylidene*-1-*cyanoacetate*-2-*carboxylate*, b. p. 152—158°/1 mm. (Found: C, 62·9; H, 6·9. $C_{14}H_{19}O_4N$ requires C, 63·4; H, 7·2%). This was reduced with aluminium amalgam, and the product hydrolysed, following Barrett, Cook, and Linstead (*loc. cit.*). The trans-1-*methyl*cyclo*pentane*-1-*carboxylic*-2-*acetic acid* (X) so obtained formed clusters of transparent prisms, m. p. 139° after three crystallisations from water (Found: C, 58·1; H, 7·8. $C_9H_{14}O_4$ requires C, 58·1; H, 7·5%). A similar mixture (200 g.) of ethyl cyanoacetate, the keto-ester, and piperidine ($\frac{1}{4}$ mol.) which had been standing for 3 years at room temperature† yielded 5 g. of condensation product, b. p. 150—160°/2 mm. By the same series of reactions this yielded a small amount of an acid, which after several crystallisations melted at 133—134°, and at 136° in admixture with the pure acid of m. p. 139° (cf. Barrett, Cook, and Linstead, *loc. cit.*).

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* Possibly the isomeric 1-carboxylic-2-β-propionic acid (XI); see p. 667.

† We are indebted to Dr. J. W. Barrett for this material.

(*b*) Ethyl 2-methyl*cyclo*pentanone-2-carboxylate (66 g.) was condensed with bromoacetic ester (34 c.c.) and magnesium (15 g.) in benzene (60 g.). After an hour's refluxing, a further 34 c.c. of bromoacetic ester were added and the reaction was completed during 2 hours on the steam-bath. The hydroxy-ester was isolated as usual (b. p. 154°/6 mm.; yield, 56%) and dehydrated with potassium hydrogen sulphate (5 hours, at 180—200°). The unsaturated ester so obtained (18 g., b. p. 150—153°/8 mm.) was reduced in acetic acid over Adams's catalyst to *ethyl* cis-1-*methyl*cyclo*pentane*-1-*carboxylate*-2-*acetate*, b. p. 140°/5 mm. (Found: C, 64·8; H, 8·5. $C_{13}H_{22}O_4$ requires C, 64·4; H, 9·2%). Hydrolysis of this ester (10 g.) with boiling hydrochloric acid for 10 hours yielded *cis*-1-methyl*cyclo*pentane-1-carboxylic-2-acetic acid (X), which melted at 108° in the crude state and at 110° after crystallisation from water. No second acid could be isolated (Found: C, 58·0; H, 7·6; equiv., 92·7. Calc. for $C_9H_{14}O_4$: C, 58·1; H, 7·5 %; equiv. 93·1). The m. p. was not depressed by the acid obtained by the oxidation of 7-methyl*bicyclo*octanone.

(*c*) The preparation of 1-methyl*cyclo*pentane-2-carboxylic-1-acetic acid (XIII) followed that by Chuang, Ma, and Tien (*loc. cit.*). The diketone (XII), obtained in 38% yield, m. p. 90—91° (lit., 92°), on oxidation with sodium hypobromite yielded the acid (XIII), m. p. 156—157° (crude), which formed glistening flattened prisms m. p. 169—170° after two crystallisations from water (lit., 166°). No second acid could be isolated.

3·5 G. of the diketone were reduced by Clemmensen's method, the product distilled in steam, and the hydrocarbon extracted from the distillate with light petroleum. The extract was washed with concentrated sulphuric acid until there was no further coloration of the acid, then with water and alkali, dried over calcium chloride, refluxed over sodium for ½ hour, and fractionated. 0·9 G. of 8-methylhydrindane was obtained, b. p. 68—70°/18 mm., $d_{4^\circ}^{18\cdot5^\circ}$ 0·8731, $n_{4^\circ}^{18\cdot5^\circ}$ 1·4688, $[R_L]_D$ 44·10 (calc., 43·98). The hydrocarbon melted at about 3° alone and at 6—8° when mixed with an equal weight of *cis*-8-methylhydrindane, m. p. 12°.

Dehydrogenations.—Materials. *trans*-Hydrindane, b. p. 159°, was made by Clemmensen reduction of *trans*-2-hydrindanone, 8-methylhydrindane, m. p. 12°, by reduction of the ketone (VI), and 8-methylhexahydroindene by dehydration of the solid alcohol (V).

Catalysts. Platinised asbestos and palladised charcoal were made by following Linstead, Millidge, Thomas, and Walpole's directions for "Platinum 1" and "Palladium 1" (*loc. cit.*, p. 1151). The palladium was purified before use through the diammino-dichloride by the method of Wichers (*Trans. Amer. Inst. Min. Eng.*, 1928, **76**, 602; cf. Keiser and Breed, *Amer. Chem. J.*, 1894, **16**, 20). The procedure followed that used in our previous work. Small quantities of indane (hydrindene) were identified as follows: 2 c.c. of concentrated sulphuric acid were added in drops to an equal volume of indane at 0°. After standing overnight, the product was poured into 1 c.c. of water and cooled in ice. The solid mass was drained on a porous tile and crystallised from 20% (vol.) sulphuric acid. This procedure yielded 84% of the trihydrate of indane-5-sulphonic acid, white plates, m. p. 92° (A. H. Cook and Linstead, J., 1934, 952).

(i) *trans*-Hydrindane (1·4 g.), passed over platinised asbestos at 310—320°, yielded 70% of the theoretical quantity of hydrogen that would have been lost by its conversion into indane. The product (0·9 g.) had $n_D^{16^\circ}$ 1·5276, and on sulphonation yielded indane-5-sulphonic acid, m. p. 92°. Over palladised charcoal at 310°, *trans*-hydrindane gave 84% of the theoretical quantity of hydrogen; the dehydrogenated product had $n_D^{17^\circ}$ 1·5401, and yielded the same sulphonic acid. When *trans*-hydrindane was refluxed in the liquid phase with palladium for 100 hours in a stream of carbon dioxide, no appreciable dehydrogenation occurred, the amount of permanent gas evolved being comparable with that from a blank experiment.

(ii) 8-Methylhydrindane (1·0 g.), passed over platinum at 330—340°, yielded only 5 c.c. of gas; the recovered hydrocarbon (0·8 g.) had the characteristic odour of the starting material and almost unchanged refractivity ($n_D^{20\cdot5^\circ}$ 1·4739). Over palladium at 330°, 1·2 g. of 8-methylhydrindane yielded 470 c.c. of gas (*ca.* 80%). The liquid product (1·0 g.) had $n_D^{19\cdot5^\circ}$ 1·5336 and on sulphonation gave pure indane-5-sulphonic acid, identified as before.

(iii) 8-Methylhexahydroindene over palladium at 330° gave 55% of the theoretical quantity of gas. The liquid product had $n_D^{18\cdot5^\circ}$ 1·5346, and gave a 70% yield of indane-5-sulphonic acid. Over platinum at 330°, the same hydrocarbon yielded no appreciable amount of gas and had $n_D^{19^\circ}$ 1·4833 after passage over the catalyst as against 1·4810 before.

Synthesis of Perhydroanthrol—To the Grignard reagent prepared from 105 g. of Δ^3-butenyl bromide, a solution of 120 g. of *trans*-2-decalone in 250 c.c. of dry ether was added slowly; the mixture was refluxed overnight and worked up in the usual manner. 75 G. of material boiling between 122° and 150°/6 mm. were obtained, which on fractionation yielded 48 g., b. p. 134—140°/5 mm.; this solidified in ice. The solid was drained on a tile and crystallised from ether at −15°, 25 g. of pure trans-2-Δ^{γ}-n-*butenyl-2-decalol* (XV) being obtained, m. p. 39° (Found: C, 80·9; H, 11·45. $C_{14}H_{24}O$ requires C, 80·7; H, 11·6%). 24 G. of the solid alcohol were cyclised during 5 days with 200 c.c. of the acetic–sulphuric acid mixture. The product was worked up and hydrolysed in the usual manner. Distillation of the neutral product yielded 12·5 g. of material, b. p. 105—120°/2 mm., which solidified in ice and was crystallised from ether. trans-cis-2-*Perhydroanthrol* (XVI) formed glistening needles, m. p. 145° (Found: C, 80·7; H, 11·45. $C_{14}H_{24}O$ requires C, 80·7; H, 11·6%). More of the same material was obtained by a similar cyclisation of liquid portions of the butenyldecalol. During the cyclisation of 5 g. of this crude alcohol with 10 c.c. of the usual reagent, some solid separated. This crystallised from ether in stout prisms, m. p. 125—126°, showed the reactions of a ketone, and yielded a semicarbazone (needles from benzene), m. p. 210—211°. It was identified as *trans*-octahydronaphthyl-*trans*-2-decalone by mixed m. p. determinations of the ketone and semicarbazone with authentic specimens (Thakur, J., 1933, 1477) and by analysis (Found: C, 83·7; H, 10·6. Calc.: C, 83·9; H, 10·55%). This substance was presumably produced by self-condensation of decalone present as impurity in the butenyldecalol.

Dehydration of 2-perhydroanthrol with its own weight of phosphoric oxide at 140° for 1 hour yielded dodecahydroanthracene, which after 30 minutes' refluxing over sodium boiled at 112—115°/15 mm. 1·2 G. of this hydrocarbon, when passed in the vapour phase over palladised charcoal at 320°, yielded 60% of the theoretical quantity of hydrogen and 0·63 g. of a fluorescent solid, m. p. 193—198°. After sublimation this had m. p. 211°, not depressed by anthracene. It was further identified by conversion into the easily dissociated picrate and into anthraquinone.

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