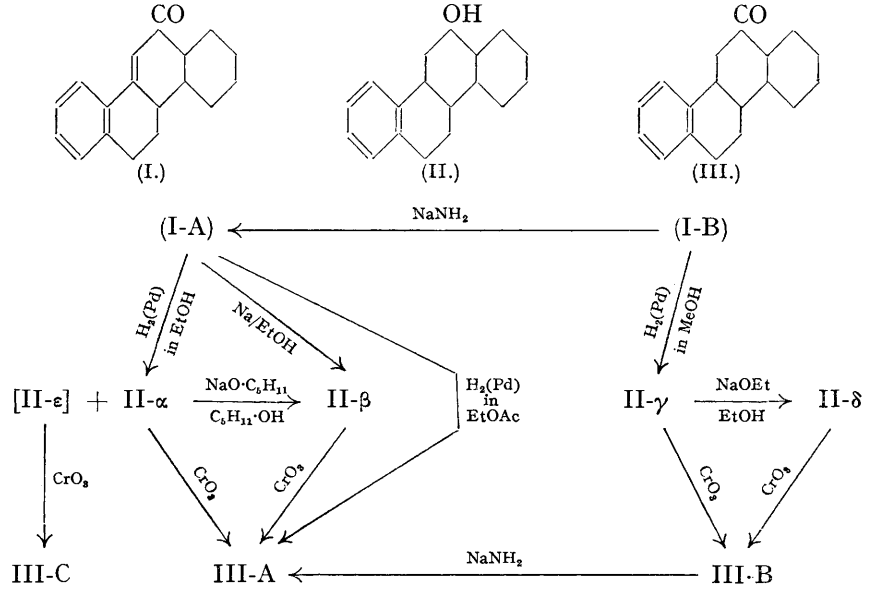
331. *Experiments on the Synthesis of Substances related to the Sterols. Part XVIII.*

By D. A. PEAK and R. ROBINSON.

The condensation of the sodio-derivative of α-tetralone with acetyl*cyclo*hexene had already been found to yield three isomeric ketodecahydrochrysenes (A, B and C), of which A and B were recognised as stereoisomerides (Peak and Robinson, J., 1936, 759). These substances and their reduction products have been further examined with the result that further stereoisomerides of the latter have been characterised. It has been found possible to *C*-methylate a ketododecahydrochrysene in the angle position and similar work has been carried out with a ketomethoxyhexahydro*cyclo*pentanophenanthrene. In this way a stereoisomeride of oestratriene methyl ether has been synthesised.

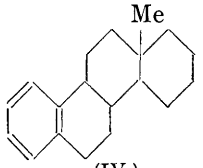
Preliminary experiments in connection with attempts to prepare *cyclo*pentane derivatives bearing the cholesterol side chain are also described.

WE have already described (*loc. cit.*) two stereoisomerides of the formula (I) (and a third structural isomeride) and two secondary alcohols of the formula (II) which yield a single



ketone (III) on oxidation. Two new stereoisomerides of the formula (II) (γ and δ) have now been isolated and these on oxidation yield a second ketone (III). The catalytic reduction of I-A affords the known II-α and other substances not yet obtained in a pure condition. Oxidation of the crude by-products, however, gives a new ketone (III) and this points to the existence of a stereoisomeride, II-ε. The scheme on p. 1581 illustrates these relations and the substances newly characterised are II-γ, II-δ, III-B and III-C.

The keto-methylene group of 2-ketododecahydrochrysene-A (III) was found to be feebly reactive towards kationoid reagents (*loc. cit.*) and hence it was thought that *C*-methylation in the angle position (16) might be realised. Using potassium *tert.*-butoxide and methyl iodide in *tert.*-butyl alcoholic-ethereal solution, we were able to isolate a *methyl* derivative, which was reduced to a *methyldodecahydrochrysene* (IV) by the Wolff–Kishner method. On dehydrogenation of this with selenium, chrysene was produced, so the methyl group is undoubtedly in position 16. This conclusion is confirmed by the difficulty experienced in effecting dehydrogenation with platinum or palladium.



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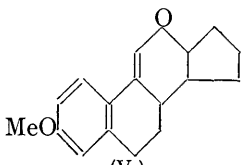

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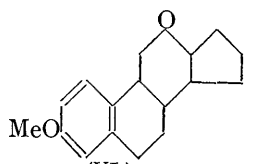
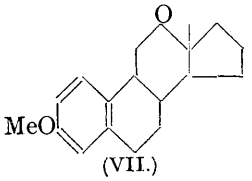


(VI.)

Rapson and Robinson (J., 1935, 1285) condensed the sodio-derivative of 6-methoxytetralone (better preparation described herein) with acetyl*cyclo*pentene and obtained 3-keto-7-methoxy-3 : 9 : 10 : 11-tetrahydro-1 : 2-*cyclo*pentanophenanthrene (V). This substance is now designated as isomeride-A, because two new isomerides-B and -C have been isolated as products of the same reaction. The absorption spectra indicate that the three substances are stereoisomerides (cf. Peak and Robinson, *loc. cit.*).

Catalytic hydrogenations of the isomerides-A and -B in ethyl acetate solution yielded the dihydro-derivatives -α and -β (VI) respectively. Both were *C*-methylated as already described and gave rise to stereoisomeric 3-*keto*-7-*methoxy*-2-*methyl*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*cyclo*pentanophenanthrenes*-α and -β (VII). The α-isomeride did not form a semicarbazone readily, but the β-form behaved normally in this respect and was reduced by the Wolff–Kishner process with production of a 7-*methoxy*-2-*methyl*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-cyclo*pentanophenanthrene* (VIII), which is a stereoisomeride of oestratriene methyl ether (Cook and Girard, *Nature*, 1937, **133**, 377). On heating with selenium this substance suffered dehydrogenation, extrusion of the methyl group, and replacement of the methoxyl group by hydrogen; the product was 1 : 2-*cyclo*pentenophenanthrene.

We are much indebted to Miss D. M. Crowfoot for crystallographic and *X*-ray examination of the substance (VIII).



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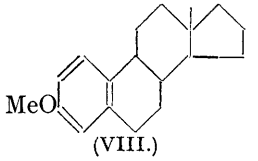
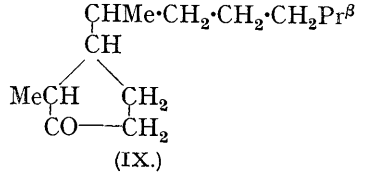


(VIII.)



(IX.)

A description of some preliminary experiments along other lines is included in this communication and the bearing of such work on the problem has been sufficiently explained in previous parts of this series of papers. A new objective is the synthesis of the ketone (IX) and some of the matter of the experimental section is connected with this.

The chief point of general interest noted was the complete failure of G. M. Robinson's keto-acid synthesis when applied to nor*dihydrocitronellic acid*, $CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$ (see p. 1591). The chloride of the acid reacted normally with ethyl sodioacetylsuccinate, but on hydrolysis of the resulting ester, no keto-acid was formed and the *nor*dihydrocitronellic acid was recovered. The investigation is being pursued along other lines.

Experimental.

2-Keto-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-dodecahydrochrysene-A (III).—2-Ketodecahydrochrysene-A (2 g.) was shaken with palladised strontium carbonate (2 g. of 2%) in dry ethyl acetate (50 c.c.) in an atmosphere of hydrogen; about 1·3 mols. of hydrogen were absorbed. The filtered solution was concentrated, and the ketonic moiety isolated as the semicarbazone (1·3 g.). This was hydrolysed without further purification by boiling for a few minutes with dilute hydrochloric acid and the solid product was crystallised from ethyl alcohol, yielding the pure ketone (0·9 g.), m. p. 147—148° (Found : C, 85·05; H, 8·4. Calc. for $C_{18}H_{22}O$: C, 85·0; H, 8·7%). The semicarbazone had m. p. 231—233°. The preparation of this ketone by the oxidation of the related secondary alcohol was described in the previous paper (*loc. cit.*), but good analytical data were never secured. The m. p. of the pure substance as now obtained is only 1° higher than formerly, but the semicarbazone melts considerably higher.

2-Keto-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-dodecahydrochrysene-C (III).—2-Ketodecahydrochrysene-A (10·8 g.) was catalytically reduced with palladised strontium carbonate in methyl-alcoholic suspension. The crude product, after removal of the catalyst and solvent, was dissolved in glacial acetic acid (100 c.c.) and oxidised in the cold with a slight excess of chromic acid. The crude ketone-A which separated was collected, and the mother-liquors again treated with chromic acid. After keeping for 2 hours, the product was isolated by means of ether and crystallised from ethyl alcohol (100 c.c.), yielding 2-ketododecahydrochrysene-A (7·3 g.), pure after a further recrystallisation. The mother-liquors, on concentration to 20 c.c., deposited a further crop (1·3 g.), which was evidently a mixture. This was converted into a mixture of oximes. On digestion with cold concentrated hydrochloric acid, the *oxime* of dodecahydrochrysene-C dissolved, leaving the oxime of the isomeride-A undissolved. The former was recovered by dilution with water and recrystallised from ethyl alcohol, separating in stout prisms, m. p. 186—187·5° (Found : C, 81·0; H, 8·5; N, 5·6. $C_{18}H_{23}ON$ requires C, 80·3; H, 8·6; N, 5·2%). The m. p. was depressed to 179—183° by admixture with the ketoxime-A. The pure oxime was hydrolysed with boiling 20% aqueous oxalic acid; the ketone obtained separated from ethyl alcohol in hexagonal prisms, m. p. 87—88° (Found : C, 85·2; H, 8·4%).

2-Hydroxy-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-dodecahydrochrysene-γ (II).—2-Ketodecahydrochrysene-B (0·1 g.) was reduced by shaking with palladised strontium carbonate (1 g.) in methyl alcohol (50 c.c.) under 3 atm. pressure of hydrogen for 10 hours. The solvent was completely removed, and the residue crystallised from aqueous ethyl alcohol, from which it separated in aggregates of small needles, m. p. 155—156° (Found : C, 84·8; H, 9·3. $C_{18}H_{24}O$ requires C, 84·4; H, 9·4%).

2-Hydroxy-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-dodecahydrochrysene-δ (II).—The above isomeride-γ (44 mg.) was heated in a sealed tube with a solution of sodium (0·1 g.) in ethyl alcohol (2 c.c.) at 100° for 6 hours. The solution was then diluted with water, and the white solid collected and crystallised from ethyl alcohol, in which it was much less readily soluble than the other isomerides. It crystallised in small needles, m. p. 162—163° (Found : C, 84·6; H, 9·6%), depressed to 153—155° by addition of the isomeride-γ.

2-Keto-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-dodecahydrochrysene-B (III).—(a) The above isomeride-γ (38 mg.) was dissolved in the least amount of pure acetic acid, and a solution (0·11 c.c.) of chromic acid (1 g.) in water (1 c.c.) and acetic acid (10 c.c.) added. After standing overnight, the solution was diluted with water, the product crystallising in small needles which after recrystallisation from aqueous acetic acid had m. p. 114—115° (Found : C, 85·5; H, 8·9%). The m. p. was much depressed by addition of either of the isomerides A and C. The oxime crystallised from ethyl alcohol in small needles, m. p. 166—167°.

(b) The isomeride-δ (18 mg.), oxidised in the same manner, gave the same ketone, as shown by m. p. and undepressed mixed m. p.

Conversion of the Ketodecahydrochrysene-B into the Isomeride-A.—Isomeride-B (50 mg.) was heated with an excess of powdered sodamide in dry benzene (10 c.c.) for 6 hours. The yellow sodio-derivative and the excess of sodamide were decomposed with water, and the benzene layer evaporated to dryness. The residue separated from ethyl alcohol in the stout needles characteristic of isomeride-A, m. p. 198—199°, undepressed by admixture with pure isomeride-A.

Conversion of the Ketododecahydrochrysene-B into the Isomeride-A.—The isomeride-B (5 mg.) was treated as above in benzene (3 c.c.). The product crystallised from aqueous alcohol in needles. The amount was insufficient for recrystallisation, but the crude substance melted at 133—135° and the m. p. was raised to 140—146° by the addition of isomeride-A, which establishes its identity.

Dodecahydrochrysene.—The previously described decahydrochrysene obtained by Wolff–Kishner reduction of the semicarbazone of ketododecahydrochrysene-A was probably not homogeneous. A repetition of the experiment furnished the expected *dodecahydrochrysene*, crystallising from ethyl alcohol in needles, m. p. 83—84° (Found: C, 89·8; H, 10·1. $C_{18}H_{24}$ requires C, 90·0; H, 10·0%).

2-*Keto*-16-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-*dodecahydrochrysene.*—Potassium (0·8 g.; 5 atoms) was dissolved in *tert.*-butyl alcohol (15 g.), and dry ether (15 c.c.) added to the cold solution. 2-Ketododecahydrochrysene-A (1 g.) was then added. On addition of methyl iodide (10 g.) to the pale yellow solution potassium iodide was almost immediately precipitated; the reaction was completed by refluxing for 1 hour. Water was then added, and the ethereal layer separated and evaporated to dryness. The residue was dissolved in ethyl alcohol (5 c.c.); the solution gradually deposited crystals (0·2 g.). This material was recrystallised from ethyl alcohol, separating in stout prisms, m. p. 122—122·5° (Found: C, 85·3; H, 9·0; *C*-Me, 3·4, 3·7. $C_{18}H_{21}MeO$ requires C, 85·1; H, 8·9; *C*-Me, 5·6%. A control analysis of the unmethylated ketone gave *C*-Me, 0·5%).

The m. p. was depressed to 106—108° by admixture with the unmethylated ketone-A and also much depressed by the addition of the stereoisomeric ketone-B. The oxime crystallised from ethyl alcohol in needles, m. p. 222—224° (mixed m. p. with ketoxime-A, 215—220°). The semicarbazone crystallised from a large volume of boiling ethyl alcohol in small needles, m. p. 245—247° (mixed m. p. with the semicarbazone of ketone-A, 228—231°).

16-*Methyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-*dodecahydrochrysene* (IV).—The above methylated ketone (1·0 g.) was converted into the semicarbazone (1·2 g.), and the latter heated for 20 hours in a sealed tube at 180° with a solution of sodium (0·8 g.) in ethyl alcohol (10 c.c.). After dilution with water, the semi-crystalline product (1·0 g.) was collected and well washed with water. The material, after distillation over sodium at 150°/3 mm., crystallised from aqueous ethyl alcohol in well-formed plates, m. p. 87—87·5° (Found: C, 89·5; H, 10·4; *C*-Me, 1·0. $C_{18}H_{23}Me$ requires C, 89·7; H, 10·3; *C*-Me, 5·9%. The corresponding unmethylated hydrocarbon gave *C*-Me, 0·6%; the low value for *C*-Me appears to be characteristic for fully saturated substances in this series). The m. p. was depressed by more than 20° by the addition of the unmethylated hydrocarbon.

Dehydrogenation of Methyldodecahydrochrysene.—(i) The hydrocarbon (50 mg.) was heated with selenium (0·25 g.) for 20 hours at 320—330°. No crystalline sublimate appeared until 10—12 hours had elapsed; the sublimate was thereafter repeatedly returned to the melt. The final crude sublimate was sublimed from sodium at 280°, yielding almost pure chrysene (10 mg.), m. p. 247—248°, alone or mixed with an authentic specimen. The *s*-trinitrobenzene complex crystallised in needles, m. p. 184—185°.

(ii) When the hydrocarbon was heated with a platinum-black of tested catalytic activity, dehydrogenation did not occur.

(iii) The hydrocarbon (0·1 g.) was heated at 300° in an atmosphere of carbon dioxide with palladised charcoal (0·1 g.) that was capable of effecting the complete dehydrogenation of the unmethylated hydrocarbon under the same conditions in 10 minutes. A crystalline sublimate appeared only after 4 hours, and gradually increased over a period of 10 hours. The sublimate, resublimed twice from palladised charcoal, melted at 247—248°, and at the same temperature when mixed with chrysene.

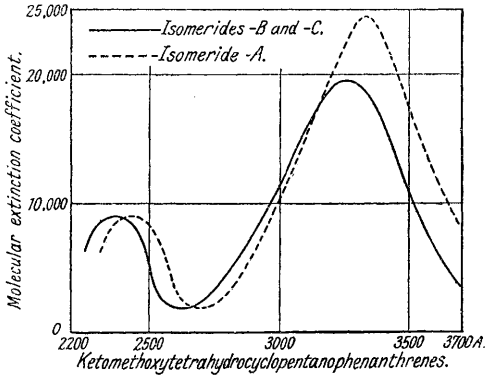
6-*Methoxy*-α-*tetralone.*—The following method of preparation of this ketone constitutes a considerable improvement on processes previously described. γ-*m*-Methoxyphenylbutyric acid (50 g.) was stirred with anhydrous stannic chloride (50 c.c.) at 100° for 1 hour. The deep red liquid was cooled and poured into cold dilute hydrochloric acid, and the resultant pale yellow oil washed free from stannic chloride by decantation, taken up in ether, and washed with dilute sodium hydroxide solution. The ethereal layer was dried over sodium sulphate and evaporated, and the residue distilled. Methoxytetralone, b. p. 130—134°/0·6 mm., sufficiently pure for most purposes, was obtained in 85—90% yield.

3-*Keto*-7-*methoxy*-3 : 9 : 10 : 11-*tetrahydro*-1 : 2-cyclo*pentanophenanthrenes-B and -C* (V).—A mixture of powdered sodamide (5·7 g.), 6-methoxy-α-tetralone (25·5 g.), and dry ether (400 c.c.) was refluxed for 7 hours with stirring in a current of dry nitrogen, after which time only traces of ammonia were present. Acetyl*cyclo*pentene (16 g.; method of Robinson and Hawthorne, J., 1936, 763) was then added dropwise with stirring and ice-cooling, and the stirring continued for 6 hours at room temperature. Next day, dilute hydrochloric acid was added, and the crystalline product collected and well washed with water, alcohol, and ether. The crude product (15·0 g.) was crystallised from ethyl alcohol (500 c.c.). The main product (isomeride-A; Rapson

and Robinson, *loc. cit.*) separated in long needles (8·3 g.), m. p. 186—187°. Two further crystallisations raised the m. p. to 194—195°.

The mother-liquors from the first crystallisation of the crude product were concentrated to *ca.* 50 c.c. On keeping, a further small amount (0·5 g.) of isomeride-A crystallised; after this had been removed, a second substance (3·8 g.) was deposited in shining plates. The substance crystallised from ethyl alcohol in needles, rapidly changing to plates, m. p. 123—124° (Found: C, 80·6; H, 7·5; OMe, 11·6. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5; OMe, 11·6%). The *substance* was much more readily soluble in most solvents than the isomeride-A.

The ethereal solution from the condensation was evaporated, and the residue dissolved in a small amount of ethyl alcohol. On keeping, the isomeride-A (1·0 g.) crystallised. The mother-liquors were diluted with water and the material recovered with the aid of ether was fractionated, yielding (i) methoxytetralone (13·0 g.), b. p. 130—150°/0·2 mm.; (ii) a yellow viscous oil (1·1 g.), b. p. 200—220°/0·2 mm., which partly crystallised in contact with ether. The crystalline material freed from oil was dissolved in hot aqueous acetic acid, from which it crystallised as a mixture of light needles (isomeride-A) and heavy, octahedral prisms. The latter were easily separated because of their greater density, which permitted the lighter needles to be swirled off. The residue (0·2 g.) crystallised from ethyl alcohol in square plates, m. p. 167—169° (mixed m. p. with isomeride-A, 154—156°) (Found: C, 80·5; H, 7·8%). The same *substance* was obtained in larger quantities by refluxing the reaction mixture for 4 hours after the addition of the acetyl-*cyclo*pentene. In this case, isomeride-B was present only in small quantities. The mother-liquors from the recrystallisation of the crude product (A), on standing, slowly deposited isomeride-C in a fairly pure condition. The absorption of the isomerides-A, -B and -C was examined in alcoholic solution (fig.).



3-*Keto*-7-*methoxy*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-cyclo*pentanophenanthrene*-α (VI).—Ketomethoxytetrahydro*cyclo*pentanophenanthrene-A (1 g.) was shaken with ethyl acetate and palladised strontium carbonate in an atmosphere of hydrogen at normal pressure. Absorption of *ca.* 1·4 mols. of hydrogen occurred slowly. The catalyst and solvent were removed, and the ketonic portion isolated as the sparingly soluble semicarbazone (0·35 g.). This was hydrolysed with boiling dilute hydrochloric acid, and the *product* crystallised from ethyl alcohol, separating in needles, m. p. 147—148° (Found: C, 80·3; H, 8·5. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2%).

3-*Keto*-7-*methoxy*-2-*methyl*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-cyclo*pentanophenanthrene*-α (VII).—Methyl iodide (7 c.c.) was added to the above isomeride-α (1·4 g.), previously dissolved in a solution of potassium (1·1 g.) in *tert.*-butyl alcohol (21 g.) and ether (21 c.c.), and the mixture was then refluxed for 1 hour. Water was added and the product, isolated by means of ether, was taken up in a little ethyl alcohol, from which it crystallised on keeping (1·05 g.). The *substance* separated from methyl alcohol in prisms, m. p. 68—69° (Found: C, 80·4; H, 8·7. $C_{19}H_{24}O_2$ requires C, 80·3; H, 8·5%). In contrast to its isomeride-β (*q.v.*), it exhibited very weak ketonic properties, the semicarbazone being particularly difficult to form.

3-*Keto*-7-*methoxy*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-cyclo*pentanophenanthrene*-β (VI).—Ketomethoxytetrahydro*cyclo*pentanophenanthrene-B (1 g.) was catalytically reduced in dry ethyl acetate solution, the absorption of hydrogen being rapid and only slightly more than the theoretical for 1 mol. of hydrogen. On removal of the ethyl acetate, the *product* crystallised; recrystallised from ethyl alcohol, it separated in long needles, m. p. 118—118·5° (Found: C, 79·8; H, 8·1; OMe, 11·5. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2; OMe, 11·5%). The *dinitrophenylhydrazone* separated from ethyl alcohol–pyridine in small, orange needles, m. p. 193—194° (Found: C, 64·1; H, 5·9. $C_{24}H_{28}O_5N_4$ requires C, 64·0; H, 5·8%).

3-*Keto*-7-*methoxy*-2-*methyl*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-cyclo*pentanophenanthrene*-β (VII).—The above isomeride-β (1 g.) was dissolved in a solution of potassium (0·8 g.) in *tert.*-butyl alcohol (15 g.) and ether (20 c.c.), and the resultant pale yellow solution refluxed with methyl iodide (5 c.c.) for 1 hour. Water was then added, and the ethereal layer evaporated to dryness. The residue was dissolved in ethyl alcohol, but no crystallisation occurred; the ketonic product was therefore isolated as the semicarbazone (0·7 g.), which was hydrolysed with

boiling dilute hydrochloric acid. The oily product was isolated with the help of ether and was dissolved in a few drops of ethyl alcohol, from which it crystallised on keeping in the ice-chest in shapely prisms (0·5 g.), which were recrystallised from light petroleum (b. p. 40—60°) and finally from methyl alcohol, separating in prisms, m. p. 75—76° (Found: C, 80·2; H, 8·6; OMe, 10·9, 10·7; *C*-Me, 6·4, 5·8. $C_{19}H_{24}O_2$ requires C, 80·3; H, 8·5; OMe, 10·9; *C*-Me, 5·3%. Control determinations on the corresponding unmethylated ketone gave *C*-Me, 1·4, 0·9%). The m. p. was lowered more than 20° by addition of the methylated isomeride-α. The *dinitrophenylhydrazone* crystallised from ethyl alcohol–pyridine in small, orange needles, m. p. 171—172°, depressed to 167—169° by admixture with the unmethylated dinitrophenylhydrazone (Found: C, 64·6; H, 6·1. $C_{25}H_{28}O_5N_4$ requires C, 64·6; H, 6·0%). The semicarbazone separated from aqueous pyridine in small prisms, m. p. 226—227°.

7-*Methoxy*-2-*methyl*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-cyclo*pentanophenanthrene* (VIII).—The saturated ketone-β (3·7 g.) was methylated as already described, and the crude semicarbazone (3·3 g.) recrystallised from aqueous pyridine, yielding practically pure semicarbazone (2·4 g.), m. p. 223—224°. Without further purification this was heated with a solution of sodium (1·6 g.) in ethyl alcohol (20 c.c.) at 180° for 20 hours. No demethylation occurred (cf. Cohen, Cook, Hewett, and Girard, J., 1934, 864). After dilution with water, the product (2·0 g.) was isolated by means of ether, and distilled from sodium. The colourless viscous distillate (1·2 g.; b. p. 183°/2 mm.) crystallised; recrystallised from methyl alcohol, it formed fine needles, m. p. 55—55·5° [Found: C, 84·0; H, 9·9; OMe, 11·6, 11·3; *C*-Me, 3·2, 2·9; *M* (*X*-ray), 275 (limits 268—280). $C_{19}H_{26}O$ requires C, 84·4; H, 9·6; OMe, 11·5; *C*-Me, 5·6%; *M*, 270].

The following *X*-ray data are due to Miss D. M. Crowfoot:

$$a = 18{\cdot}0\ (\alpha),\ b = 7{\cdot}16\ (\beta),\ c = 25{\cdot}0\ (\gamma);\ n = 8;\ \rho = 1{\cdot}13 \pm 0{\cdot}03.$$

For comparison the cell dimensions of the stereoisomeric optically active compound obtained by reduction of oestrone methyl ether are:

$$a = 11{\cdot}4,\ b = 7{\cdot}15,\ c = 19{\cdot}25;\ n = 4.\quad \text{Space group } P2_12_12_1.$$

No great accuracy is claimed for the latter values. We are greatly indebted to Professor J. W. Cook for the provision of a specimen of methoxymethylhexahydro*cyclo*pentanophenanthrene prepared by him from oestrone.

*Dehydrogenation of Methoxymethylhexahydro*cyclo*pentanophenanthrene.*—The substance (1·6 g.) was heated in a sealed tube with selenium (3 g.) at 300—320° for 5 days, the tube being opened and resealed from time to time. The dark product was taken up in ether, and the residue finely ground and extracted (Soxhlet) with benzene. The combined benzene and ethereal extracts were evaporated to dryness, and the residue distilled. The colourless product (1·0 g.; b. p. 150—170°/0·1 mm.) partly crystallised on cooling. Analysis suggested that the substance was *cyclo*pentenophenanthrene contaminated with a little 7-methoxy*cyclo*pentenophenanthrene. It was therefore heated with acetic acid (10 c.c.) and hydriodic acid (10 c.c.) for 4 hours, diluted with water, recovered with the use of ether, and distilled from sodium. The colourless distillate (0·7 g.; b. p. 165—172°/1 mm.) crystallised on cooling and after recrystallisation from methyl alcohol the product (0·15 g.) was converted into the *s*-trinitrobenzene complex. This was thrice crystallised from methyl alcohol (yellow needles) and had m. p. 164·5—165°, not depressed by admixture with an authentic specimen of *cyclo*pentenophenanthrene *s*-trinitrobenzene complex (Found: C, 64·0; H, 4·1. Calc. for $C_{23}H_{17}O_6N_3$: C, 64·0; H, 4·0%). The hydrocarbon, regenerated from the complex by treatment with alcoholic stannous chloride, crystallised from ethyl alcohol in needles, m. p. 135°, alone or mixed with pure *cyclo*pentenophenanthrene prepared by the method of Cook and Hewett (J., 1933, 1098). The removal of a methoxyl group situated in the benzene nucleus in this reaction is of considerable interest and may prove within limits to be a general reaction. The reducing agent is considered to be hydrogen selenide and the essentials would appear to be selenium and a hydroaromatic substance at an elevated temperature. Using tetralin as a source of hydrogen, it has already been found that selenium acts partly at least as a catalyst and some difficult reductions have been effected. It is hoped that an account of the scope of this method may shortly be submitted.

7-*Hydroxy*-3-*keto*-3 : 9 : 10 : 11-*tetrahydro*-1 : 2-cyclo*pentanophenanthrene.*—3-Keto-7-ethoxy-3 : 9 : 10 : 11-tetrahydro-1 : 2-*cyclo*pentanophenanthrene (1·0 g.; Hawthorne and Robinson, *loc. cit.*) was refluxed with aluminium bromide (3·0 g.) in purified benzene (50 c.c.) for 4 hours. The resulting liquid complex was decomposed with dilute hydrochloric acid and the almost colourless solid (0·5 g.) was collected and crystallised from ethyl alcohol, separating in fine needles, m. p. 249° (Found: C, 80·5; H, 7·3. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%). It gave

no ferric reaction, but was soluble in hot dilute sodium hydroxide solution, from which the sparingly soluble yellow sodium salt crystallised in needles on cooling.

7-*Hydroxy*-3-*keto*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-cyclo*pentanophenanthrene*.—The foregoing substance (0·3 g.) was catalytically reduced in ethyl-alcoholic solution at normal pressure, palladised strontium carbonate being used. Hydrogen in slight excess of 1 mol. was rapidly absorbed. The catalyst and solvent were removed, the residue dissolved in dilute aqueous sodium hydroxide, and the solution boiled with charcoal for 1 hour. The cold filtered solution was acidified with acetic acid, and the white solid collected and crystallised from ethyl alcohol forming small needles, m. p. 187—189° (decomp.) (Found : C, 79·8; H, 7·8. $C_{17}H_{20}O_2$ requires C, 79·7; H, 7·8%).

3-*Keto*-1-*furyl*-2-*methyl*-1 : 2 : 3 : 9 : 10 : 11-*hexahydrophenanthrene*.—(A) Sodio-α-tetralone was prepared by refluxing a mixture of tetralone (10 g.), sodamide (2·8 g.), and dry ether (200 c.c.) with stirring in an atmosphere of dry nitrogen for 5 hours. β-Furyl*iso*propenyl methyl ketone (10·3 g.; b. p. 117—120°/10 mm.) in ether (20 c.c.) was then added dropwise at − 10° to − 12° with stirring, which was continued for 5 hours at room temperature. After keeping overnight, the crystalline product was collected and recrystallised from ethyl alcohol, from which it separated in long, colourless prisms (1·2 g.), m. p. 137·5—138° (Found : C, 82·1; H, 6·7. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%). A further quantity (2·5 g.) of the same substance was obtained by concentration of the ethereal layer from the initial condensation.

(B) α-Tetralone (10 g.) in ether (200 c.c.) was added to a solution of potassium (2·8 g.) in *tert.*-butyl alcohol (33 g.), and the clear red solution cooled to − 15°. Furyl*iso*propenyl methyl ketone (10·3 g.) in ether (20 c.c.) was then introduced at such a rate that the temperature did not rise above −10°. Towards the end of the addition, crystals appeared around the neck of the flask. Stirring was continued at room temperature for 3 hours; water was then added, the product extracted with ether, the extract washed with dilute aqueous sodium hydroxide and evaporated, and the residual dark oil seeded. Crystallisation slowly ensued, yielding the same substance (1·3 g.) as in (A) but in much inferior yield.

3-*Hydroxy*-1-*furyl*-2-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*.—The foregoing substance (3·0 g.) in methyl alcohol (100 c.c.) was shaken with palladised strontium carbonate (2 g. of 2%) at 3 atms. pressure of hydrogen for 15 hours. The residue crystallised after removal of the catalyst and solvent; recrystallised from light petroleum (b. p. 60—80°), it separated in flocculent needles (2·1 g.). A portion recrystallised from aqueous ethyl alcohol formed long, fine needles, m. p. 140—140·5° (Found : C, 80·5; H, 7·9. $C_{19}H_{22}O_2$ requires C, 80·8; H, 7·8%).

An attempt to open the furyl ring was made in that the finely powdered substance was shaken with an excess of bromine water in the cold for 24 hours. The heavily brominated product was acidic but amorphous and all attempts to remove the bromine either by catalytic reduction or with sodium and ethyl alcohol were unsuccessful.

3-*Keto*-1-*methyl*-1 : 2 : 3 : 9 : 10 : 11-*hexahydrophenanthrene*.—(A) Sodio-α-tetralone was prepared as previously described from α-tetralone (10 g.), sodamide (2·8 g.), and ether (200 c.c.). The flask was then cooled in a freezing mixture, and ethyl ethylideneacetoacetate (10·8 g.; b. p. 97—99°/14 mm.) in ether (50 c.c.) added dropwise with stirring. Stirring was continued for 3 hours at 0°, and the mixture left overnight. It was then decomposed with ice and dilute hydrochloric acid, the ethereal layer dried (sodium sulphate) and evaporated, and the residue fractionated under reduced pressure. After a small low-boiling fraction (1·2 g.) up to 115°/15 mm., tetralone (5·6 g.) was collected at 94—140°/1 mm., and then a third fraction (5·2 g.; b. p. 160—190°/1 mm., practically all 181—190°), which crystallised in the receiver. It was recrystallised from light petroleum (b. p. 60—80°) or aqueous ethyl alcohol and obtained in plates, m. p. 119—120° (Found : C, 84·7; H, 7·6. $C_{15}H_{16}O$ requires C, 84·9; H, 7·5%). The substance gave no coloration with alcoholic ferric chloride.

(B) The condensation was also effected with potassium *tert.*-butoxide, but as in the previous case the yield was much inferior to that obtained with sodamide.

The p-*Phenylphenacyl Ester of* γ-*Carboxypropylideneacetone*.—Ethyl γ-carbethoxypropylideneacetoacetate (38 g.; Peak, Robinson, and Walker, J., 1936, 754) was boiled with 10% hydrochloric acid (100 c.c.) until it passed completely into solution (2 hours). During the hydrolysis a considerable volume of carbon dioxide was evolved. The hydrochloric acid was then removed under reduced pressure; the residue (17·5 g.) distilled as a colourless liquid, b. p. 160—166°/13 mm. This acid rapidly decolorised aqueous alkaline permanganate solution. The p-*phenylphenacyl* ester, prepared in the usual manner, separated from ethyl alcohol in needles, m. p. 93—94° (Found : C, 74·8; H, 6·1. $C_{21}H_{20}O$ requires C, 75·0; H, 6·0%).

Condensation of α-*Tetralone and Ethyl* γ-*Carbethoxypropylideneacetoacetate*.—Sodio-α-tetralone

prepared from tetralone (10 g.), sodamide (2·8 g.), and ether (200 c.c.) was cooled in a freezing mixture, and ethyl γ-carbethoxypropylideneacetoacetate (16·7 g.) in ether (50 c.c.) added dropwise with stirring. The reaction mixture was stirred for 4 hours at 0° and left overnight. It was decomposed with ice and dilute hydrochloric acid, and the ethereal layer washed with dilute aqueous sodium carbonate, which removed most of the colour. The dried ethereal solution was evaporated and on fractionation there were obtained: (i) b. p. up to 110°/14 mm. (2 g.), a colourless liquid with a red ferric reaction and an odour similar to that of ethyl acetoacetate; (ii) b. p. 120—140°/14 mm. (5·5 g.), unchanged tetralone; (iii) b. p. 190—200°/0·8 mm. (6·65 g.). The last fraction was a pale yellow, fairly mobile liquid giving a strong violet ferric reaction and a positive test for an aromatic nucleus (nitration and eventual formation of an azo-compound). It was evidently a mixture, since extraction of its ethereal solution with 10% aqueous sodium hydroxide removed an acidic substance (see below) and the material on recovery by distillation then exhibited no ferric reaction. Analytical results did not tally with the expected values (Found: C, 69·5, 69·5; H, 7·3, 7·4; OEt, 20·0. $C_{19}H_{22}O_3$ requires C, 72·2; H, 7·6; OEt, 15·1%). On treatment with Brady's reagent, however, the substance slowly yielded a solid derivative, which was crystallised repeatedly from ethyl alcohol and from acetic acid, separating in red prisms, m. p. 183—184° (Found: C, 60·5; H, 5·0; N, 11·9; OEt, 8·5. $C_{25}H_{28}O_7N_4$ requires C, 60·7; H, 5·3; N, 11·4; OEt, 9·1%). It may be suggested that this substance is an azo-derivative formed by addition of dinitrophenylhydrazine to the double bond of the anticipated product and oxidation.

The acidic *substance* obtained by acidification of the sodium hydroxide washings was purified by trituration with ether, which removed all the colour, and by crystallisation from boiling water, from which it separated in colourless needles, m. p. 202·5—203·5° after sintering at 196° (Found: C, 57·5; H, 5·0; OEt, 15·0. $C_{14}H_{14}O_7$ requires C, 57·1; H, 4·8; OEt, 15·4%). The substance was easily soluble in dilute sodium carbonate solution and was reprecipitated by hydrochloric acid. It gave an intense red ferric reaction and was insoluble in non-hydroxylic solvents. The constitution of this acid has not been determined, but it appears to be ketonic. The *dinitrophenylhydrazone* crystallised from ethyl alcohol in orange needles, m. p. 205—207° (Found: C, 50·2; H, 4·8; N, 11·1. $C_{20}H_{18}O_{10}N_4,C_2H_6O$ requires C, 50·6; H, 4·6; N, 10·8%). The substance was easily soluble in sodium hydroxide and gave no ferric reaction.

Attempted Condensation of 6-Methoxy-α-tetralone and Ethyl γ-Carbethoxypropylideneacetoacetate.—The sodio-derivative of the ketone (7·3 g.) was made as usual in ether (140 c.c.), and the unsaturated ester (10 g.) in ether (30 c.c.) then added. After standing overnight, the product was worked up as before. Methoxytetralone (5·4 g.) was recovered, and a small fraction (1·7 g.; b. p. 210—214°/0·7 mm.) obtained as a viscous yellow oil. No crystalline derivatives could be obtained and in view of the unfavourable yield the condensation was not further investigated.

Ethyl γ-Phenylpropylideneacetoacetate.—A mixture of ethyl acetoacetate (10 g.), β-phenylpropaldehyde (10·3 g.), and acetic anhydride (15 g.) was heated for 24 hours at 100°. The acetic anhydride was then removed under reduced pressure, and the residue fractionated. After a small amount of unchanged material, the main fraction was collected at 145—160°/0·35 mm. (16·5 g.). After redistillation (b. p. 140—143°/0·1 mm.), it had $n_D^{15°}$ 1·5241 and gave no ferric reaction (Found: C, 72·7; H, 7·0. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%).

Attempted Condensation of the Foregoing with α-Tetralone.—Sodio-α-tetralone was prepared as previously from tetralone (3·7 g.) in ether (100 c.c.). After cooling to −15°, ethyl γ-phenylpropylideneacetoacetate (6·4 g.) in ether (20 c.c.) was added dropwise, and the mixture stirred for 4 hours and left overnight. After decomposition with dilute hydrochloric acid, there remained a small amount of insoluble solid, which was collected. It crystallised from ethyl alcohol in colourless shining plates, m. p. 130·5—131° (Found: C, 88·6; H, 7·5%). Although this was undoubtedly a pure substance, the analysis does not confirm our anticipations. The residual, ether-soluble product yielded on fractionation unchanged tetralone (2·6 g.) and a viscous yellow oil (2·8 g.; b. p. 205—245°/1 mm., decomp.). The material was obviously a mixture and could not be induced to yield any crystalline derivative.

Ethyl 2-Methylcyclopentanone-3-carboxylate.—The method of Haworth and Perkin (J., 1908, **93**, 581) has been slightly modified. (i) Ethyl cyano-2-methylsuccinate was obtained in 70% yield exactly as described by Bone and Sprankling (J., 1899, **75**, 853). The observed b. p. was, however, 150—153°/17 mm., not 160—165°/17 mm. as stated by these authors.

(ii) The ester (112 g.) was added to a cold solution of sodium (12·1 g.) in absolute alcohol (200 c.c.), and ethyl β-chloropropionate (71·8 g.) added dropwise, the temperature being kept below 25°. Next day, the mixture was heated for 1 hour on the steam-bath. Worked up in the usual way, it yielded 148 g. (90%) of the pure product, b. p. 160—165°/3 mm. If ethyl

malonate is substituted for ethyl cyanoacetate in this series of processes, a very poor yield is obtained at this stage.

(iii) Ethyl 3-cyanopentane-2 : 3 : 5-tricarboxylate (148 g.) was refluxed with concentrated hydrochloric acid (3 vols.) and the alcohol formed was distilled through a refluxing fractionating column until solution was complete. The solution was concentrated by distillation until ammonium chloride began to separate and then evaporated to dryness on the steam-bath. The solid cake of ammonium chloride and pentane-2 : 3 : 5-tricarboxylic acid was heated with absolute alcohol (300 c.c.), carbon tetrachloride (240 g.), and concentrated sulphuric acid (30 c.c.) under an efficient fractionating column, through which the azeotropic mixture of alcohol, carbon tetrachloride, and water was slowly distilled. A mixture of equal volumes of alcohol and carbon tetrachloride was added at the same rate as the distillate was removed. The process was continued until the distillate no longer clouded on cooling (*ca.* 30 hours with a very slow rate of distillation). The product, recovered in the usual way, distilled at 146—149°/3 mm. (yield, 81%, over-all from the cyano-ester).

(iv) The foregoing ester (110 g.) was added slowly to dry, powdered sodium ethoxide (30 g.) in dry ether (200 c.c.). The mixture became warm and the sodium ethoxide passed into solution. After refluxing for 2 hours, dilute hydrochloric acid was added, and the ethereal layer washed with dilute aqueous sodium carbonate, which removed most of the colour. (These washings were acidified with hydrochloric acid and refluxed for 4 hours. The cold solution was then extracted with the ether to be used in the first extractions of the next stage.) After the ethereal solution had been dried (sodium sulphate), the ether was evaporated, and the residue distilled, b. p. 143—148°/6 mm. (71 g. or 77%).

(v) 2-Methyl*cyclo*pentanone-3-carboxylic acid was obtained by hydrolysis of the foregoing substance in the known manner, except that the alcohol resulting from the hydrolysis was removed by slow distillation through a fractionating column. The white crystalline acid thus obtained had b. p. 147—149°/3 mm. (97% yield).

The acid (40·2 g.) was esterified by the above-described method. The ester had b. p. 116—118°/16 mm. (40·0 g. or 83%).

Attempted condensations of this ester with diethylaminobutanone methiodide by means of dry sodium ethoxide in ether at −10° or of potassium *tert.*-butoxide in ether and *tert.*-butyl alcohol gave negative results in both cases. Most of the material was converted into resinous high-boiling substances.

Diethylamide of 2-*Methyl*cyclo*pentanone*-3-*carboxylic Acid.*—The acid (10·2 g.) was dissolved in ether (40 c.c.) and dry pyridine (5·7 g.), and thionyl chloride (8·6 g.) added dropwise with ice-cooling. Pyridine hydrochloride first separated crystalline but later became dark and oily. After keeping overnight, the ether was decanted, and a solution of diethylamine (12 g.; 2 mols.) in ether (20 c.c.) added slowly. After refluxing for 1 hour, the mixture was poured on the pyridine hydrochloride residue, and the whole well shaken and refluxed for a short time. Water was then added, and the ethereal layer dried. There was obtained by distillation a fraction (4·5 g.), b. p. 132—135°/0·5 mm., and on redistillation 117—119°/0·1 mm. (Found: N, 6·8. $C_{11}H_{19}O_2N$ requires N, 7·1%). The *dinitrophenylhydrazone* crystallised from ethyl alcohol in glistening orange plates, m. p. 199—199·5° (Found: C, 54·5; H, 6·2; N, 18·5. $C_{17}H_{23}O_5N_5$ requires C, 54·1; H, 6·1; N, 18·6%).

6-*Methylheptan*-2-*ol.*—6-Methylheptan-2-one (101 g.), obtained in almost theoretical yield by the catalytic reduction of methylheptenone, was heated under an efficient fractionating column with aluminium *iso*propoxide (53 g.; 1/3 mol.) and dry *iso*propyl alcohol (200 c.c.). Acetone, which was freely evolved, was gradually distilled and replaced by fresh *iso*propyl alcohol until acetone could not be detected in the distillate. The excess of *iso*propyl alcohol was evaporated as completely as possible, and the residue decomposed with dilute hydrochloric acid and extracted with ether. The extract was dried and evaporated, and the residue distilled, giving pure methylheptanol (95·5 g.), b. p. 78—81°/16 mm., $n_D^{19°}$ 1·4273.

2-*Chloro*-6-*methylheptane.*—A mixture of methylheptanol (20 g.), dimethylaniline (18·6 g.), and dry chloroform (40 c.c.) was cooled in ice, and thionyl chloride (18·3 g.) in chloroform (10 c.c.) added dropwise. The solution was refluxed for 2 hours, water added, and the chloroform layer dried. The chloroform was distilled through a fractionating column, and the residue distilled. The fraction, b. p. 57—63°/15 mm. (16·7 g.), was freed from unchanged alcohol by cooling to 0° and shaking with cold concentrated sulphuric acid. After washing with water, it was redistilled, yielding the pure product, b. p. 74—75°/35 mm., $n_D^{15°}$ 1·4260 (Found: C, 64·4; H, 11·4; Cl, 24·0. $C_8H_{17}Cl$ requires C, 64·7; H, 11·4; Cl, 23·9%). A Grignard solution was prepared from the *chloride* (10·2 g.) and activated magnesium (1·7 g.) in ether (100 c.c.), but only with

great difficulty. The solution had to be heated continuously and a considerable quantity of magnesium chloride was produced. The cold solution was added slowly to ethyl β-formylpropionate (8·0 g.) in ether (10 c.c.) at 0°. A little complex was precipitated. Worked up in the usual way, the product yielded, besides low-boiling fractions (4·1 g.), a small fraction (2·7 g.), b. p. 117—120°/1 mm. This, however, was not lactonic in nature and because of the poor yield was not further investigated. An estimation of the percentage of organomagnesium compound formed (carbon dioxide on the cold solution and titration of the acid formed) gave as a maximum value, 41%.

2-*Iodo*-6-*methylheptane*.—Methylheptanol (20 g.) was mixed with red phosphorus (2 g.), and iodine (20 g.) added in portions with shaking. After standing overnight at room temperature, the mixture was heated at 100° for 2 hours. The product was then distilled (b. p. 72—78°/14 mm.), taken up in chloroform (50 c.c.), the free iodine removed by washing with aqueous sodium thiosulphate, and the colourless solution dried. It was then cooled to − 10°, shaken with concentrated sulphuric acid (½ vol.)also cooled to − 10°, washed with water, dried, and evaporated. The residue distilled at 83°/14 mm. (31 g.) (Found: C, 41·0; H, 7·5. $C_8H_{17}I$ requires C, 40·0; H, 7·1%). It was a heavy, colourless, mobile liquid, $n_D^{17°}$ 1·4870.

Reaction of magnesium (2 g.) in ether (10 c.c.) was initiated with methyl iodide (0·5 g.), and a solution of the iodide (20 g.) in ether (75 c.c.) added dropwise. The reaction proceeded smoothly and was completed by refluxing for 15 minutes; a considerable quantity of magnesium, however, remained undissolved. The solution was added to ethyl β-formylpropionate (10 g.) in ether (75 c.c.) at 0°. Only a small amount of complex was precipitated. After shaking for 15 minutes, the product was worked up as usual. There were obtained: (i) unchanged iodide (5 g.); (ii) b. p. 103—108°/3 mm. (3·2 g.), a colourless liquid insoluble in boiling caustic soda solution and immiscible with alcohol and therefore probably 2 : 6 : 7 : 11-tetramethyldodecane; (iii) b. p. 134—144°/3 mm. (1 g.), not a lactone and therefore not further investigated; (iv) a very high-boiling residue.

Note.—No success was achieved in attempts to introduce the residues of ethyl α-bromopropionate and ethyl β-chloropropionate into ethyl acetoacetate. In whichever order the condensations were carried out, the second did not take place.

Δ^1-*Dihydrocitronellylideneacetic Acid*.—Dihydrocitronellal (26 g.; b. p. 76—79°/12 mm.; $n_D^{17°}$ 1·4281) was heated with malonic acid (18 g.), pyridine (40 c.c.), and piperidine (1 c.c.) at 100° for 6 hours. During the first hour there was a copious evolution of carbon dioxide. The mixture was then poured into aqueous sodium hydroxide (100 c.c. of 10%), extracted with ether, acidified, and the oil extracted with ether. The product had b. p. 158—161°/12 mm., $n_D^{14°}$ 1·4590 (25·6 g.).

Prolonged treatment with boiling 62% sulphuric acid failed to effect any lactonisation (cf. Fittig, *Annalen*, 1894, **283**, 51).

Δ^8-*Dihydrocitronellylideneacetic Acid*.—Citronellylideneacetic acid (13 g.; Rupe, Pfeiffer, and Splittgerber, *Ber.*, 1907, **40**, 2813) was dissolved in aqueous sodium hydroxide (100 c.c. of 1%) and heated at 100° for 12 hours with sodium amalgam (500 g. of 3%). During the latter part of the reduction, the mixture was vigorously stirred. The alkaline layer was acidified and extracted with ether, and the extract evaporated. The product (11 g.), b. p. 162—166°/12 mm., $n_D^{15°}$ 1·4668, was only partly reduced (Found: C, 73·0; H, 10·6. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·1%. $C_{12}H_{20}O_2$ requires C, 73·5; H, 10·2%).

On treatment with concentrated sulphuric acid at 80° (cf. Shukow and Schestakow, *Chem. Zentr.*, 1908, II, 1414) this material was completely polymerised. No trace of lactone could be isolated.

Ethyl Δ^1-*Dihydrocitronellylideneacetate and its Condensation with Ethyl Oxalate*.—Dihydrocitronellylideneacetic acid (37 g.) was refluxed for 10 hours with ethyl alcohol (150 c.c.) and concentrated sulphuric acid (10 c.c.). The *ester*, isolated in the usual way, distilled at 128—131°/10 mm. (36 g.) (Found: C, 74·3; H, 11·5. $C_{14}H_{26}O_2$ requires C, 74·3; H, 11·5%).

Powdered potassium (3·0 g.) was added to ethyl oxalate (10·7 g.) in benzene (100 c.c.). The above ester (16·5 g.) was then added slowly. A moderately vigorous reaction soon set in, the benzene finally boiling and the solution becoming deep red. Next day the mixture was decomposed with dilute acetic acid, and the benzene layer dried and evaporated. The residue, which gave a deep red ferric reaction, could not be distilled even at 0·006 mm. without decomposition. The crude material (11·0 g.) was therefore catalytically reduced in alcoholic solution, *ca.* two-thirds of the theoretical volume of hydrogen being absorbed. Decomposition still occurred on attempted distillation at 0·006 mm., the vacuum falling to 1 mm. At this pressure there was obtained a fraction (3 g.), b. p. 150—160°/1 mm., redistilling

at 131—136°/0·4 mm. (Found : C, 68·1; H, 10·8. $C_{17}H_{32}O_4$ requires C, 68·0; H, 10·7%). Evidently therefore carbon monoxide had been evolved during distillation.

Attempted Synthesis of β-nor*Dihydrocitronelloylpropionic Acid.*—(i) *Dihydrocitronellic acid.* Dihydrocitronellal (76·5 g.) was mixed with pure acetic acid (200 g.), and a solution of chromic acid (34 g.) in water (25 c.c.) added dropwise so that the temperature remained at *ca.* 50°. After standing for 12 hours, water and concentrated hydrochloric acid (100 c.c.) were added and the product was extracted with ether and distilled at 130—135°/10 mm. (63·0 g.).

(ii) *Ethyl dihydrocitronellate.* The acid (63 g.) was heated on the water-bath for 1 hour with thionyl chloride (50 g.). Excess of ethyl alcohol (50 c.c.) was added to the cold solution, and the mixture refluxed for 2 hours. It was then diluted with water, the oil extracted with ether, and the extract washed with dilute aqueous sodium carbonate and evaporated. The residue distilled at 98—100°/10 mm. (67·4 g.).

(iii) 8 : 8-*Diphenyl*-2 : 6-*dimethyl*-Δ^7-*octene.* Ethyl dihydrocitronellate (67 g.) was added dropwise to a Grignard solution prepared from bromobenzene (158 g.) and magnesium (24 g.) in ether (500 c.c.). There was a vigorous reaction, but no complex was precipitated. After refluxing for 2 hours, the ether was distilled, and the residue heated for 6 hours at 100°. It was then decomposed with dilute hydrochloric acid, and the resulting oil isolated with ether. On fractionation, after the distillation of a small amount of diphenyl, there was obtained a pale yellow oil, b. p. 150—157°/0·6 mm. (92 g.), immiscible with all hydroxylic solvents.

(iv) nor*Dihydrocitronellic acid.* The hydrocarbon (70 g.) was emulsified with acetic acid (400 c.c.) by stirring, and solid chromic acid (75 g.) added in small portions so that the temperature remained at 50—60°. When the solution had cooled, water and concentrated hydrochloric acid (225 c.c.) were added. An ethereal extract of the product was washed with water and evaporated, and acetic acid distilled through a short fractionating column. The residue was added to 10% aqueous sodium hydroxide (100 c.c.), and the benzophenone extracted with ether. The alkaline solution was acidified, and the product isolated by means of ether. On fractionation practically the whole distilled at 127—129°/10 mm. (22·8 g. or 60%) (Found : C, 68·3; H, 11·4. $C_9H_{18}O_2$ requires C, 68·3; H, 11·4%).

(v) *nor*Dihydrocitronellic acid (25·8 g.) was heated for 2 hours with thionyl chloride (26 c.c.). The excess of thionyl chloride was then removed under reduced pressure, and the residue distilled, yielding *nor*dihydrocitronelloyl chloride (26·5 g.), b. p. 71—71·5°/8 mm.

Sodium (3·5 g.) was powdered under toluene and washed with ether, and ether (180 c.c.) added. Ethyl acetosuccinate (32·5 g.) was then added, and the vigorous reaction completed by heating on the steam-bath for 1 hour. The chloride (26·5 g.) in ether (30 c.c.) was added dropwise at 0° to the clear solution of ethyl sodioacetosuccinate. Gelatinous sodium chloride was precipitated and after 12 hours the reaction was completed by refluxing for 1 hour. Water was added, and the ethereal layer washed with dilute aqueous sodium carbonate (no unchanged acid on acidification). The ether was evaporated, and the residue stirred vigorously for 24 hours with 4·5% aqueous potassium hydroxide solution (1 l.). The small amount of unhydrolysed material was extracted with ether, and the alkaline layer acidified with sulphuric acid and saturated with ammonium sulphate. The liberated oil was extracted ten times with ether, the ether removed, and the residue heated at 140° for 2 hours. 10% Sodium hydroxide solution (300 c.c.) was then added, and the solution refluxed for 5 hours. After acidification the liberated oil was isolated with ether. On fractionation of the product, *nor*dihydrocitronellic acid (22·0 g.) was recovered, there being no significant residue. A repetition of the experiment using a shorter period of hydrolysis gave the same result.

When a specimen of acid which undoubtedly contained some dihydrocitronellic acid was used a small amount of a keto-acid was obtained, b. p. 175—188°/5 mm. The *semicarbazon*, crystallised from ethyl alcohol in laminated plates, m. p. 156—157° (Found : C, 59·2; H, 9·2; N, 15·0. $C_{14}H_{27}O_3N_3$ requires C, 59·6; H, 9·5; N, 14·8%). Hence this substance is derived from dihydrocitronellic acid and not from the *nor*-compound.

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