Experiments on the Synthesis of Substances Related to the Sterols. Part LII. Some Condensations of Substituted β-Diketones including an Account of a New Molecular Rearrangement.*

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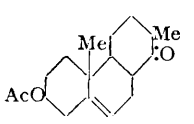
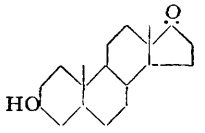
Model experiments designed to test a possible method of adding ring D to an ABC-tricyclic system, such as is found in a steroid degradation product, are described. Two stages of acetylation of ketones R·CHMe·COR′ with acetic anhydride and boron trifluoride afforded R′·CO·CMeR·CO·CH_2·COMe in poor yield. Efforts to cyclise these triketones were unsuccessful.

Condensation of 2-methyl-*trans*-1-decalone with 1 : 3-dichlorobut-2-ene, followed by cyclisation, gave a BCD-tricyclic ketone. Reduction of the double bond by various methods invariably resulted in a *cis*-C/D-junction.

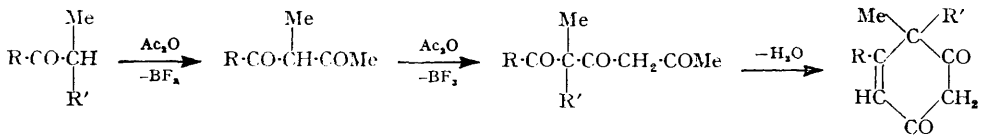
α-Acetyl*iso*butyrophenone was converted by sodium in ethereal medium into ω-*iso*butyrylacetophenone (1 : 3-dioxo*iso*hexylbenzene). This molecular rearrangement has not been previously observed among straight-chain compounds. It is analogous to certain transformations of cyclic keto-esters and to the Baker–Venkataraman change.

THE isolation of the ABC-tricyclic keto-acetate (I) as a steroid oxidative degradation product by Köster and Logemann (*Ber.*, 1940, **73**, 298) stimulated investigations of the possibility of adding ring D to such a system, so as to regenerate the steroid framework as in androsterone

(I)   (II)

(II). The present communication describes investigations, with model ketones, of a new possible method of fusion of a ring D to an ABC-tricyclic system, but the outcome was not encouraging.

Meerwein and his co-workers (*Ber.*, 1933, **66**, 411; *J. prakt. Chem.*, 1934, **141**, 149) and Adams and Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 345; 1945, **67**, 284) have shown that ketones containing reactive ≥CH, >CH_2, or —CH_3 groups can be acylated with acid anhydrides and boron trifluoride with formation of the corresponding α-acyl-ketones. We contemplated the use of this reaction to provide a six-membered ring (which might be degraded to a five-membered ring) as shown in the following scheme, using acetic anhydride as acylating agent :

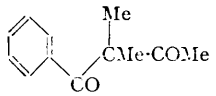


Several α-methyl-ketones have been used as models in these reactions. We have confirmed that, in the presence of boron trifluoride, the corresponding α-acetyl-α-methyl-ketone can be obtained in moderate yield.

*iso*Butyrophenone afforded α-acetyl*iso*butyrophenone (III); and further acetylation of this diketone gave 5-benzoyl-5-methylhexane-2 : 4-dione (IV), but in very poor yield.

* Part LI, *J.*, 1953, 361. The results reported in the present paper formed part of a Thesis (A. R. P.) submitted in May, 1950.

A small quantity of the latter substance was isolated from the reaction mixture in the first stage of acetylation; in fact, in every case we have examined, a small quantity of the triketone accompanied the monoacetylated ketone.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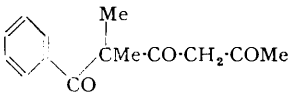
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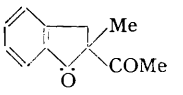
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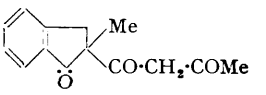
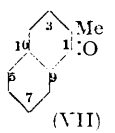

(VI)

The acetylation in this manner of 2-methylindan-1-one afforded 2-acetyl-2-methylindan-1-one (V) and 2-acetoacetyl-2-methylindan-1-one (VI), the latter in very poor yield. Similarly, 2-methyl-*trans*-1-decalone (VII) gave 2-acetyl-2-methyl-*trans*-1-decalone (VIII), and further acetylation gave 2-acetoacetyl-2-methyl-*trans*-1-decalone (IX). There is, in the case of 2-methyl-*trans*-1-decalone, some doubt about the position taken up by the first acetyl group, as the ketone has an angular $\geqslant$CH group adjacent to the carbonyl group. From steric considerations, we are of the opinion that the acetyl group has entered the 2-position, but the possibility that the product contains some 9-acetyl-2-methyl-*trans*-1-decalone (X) cannot be ruled out since Adams and Hauser (*loc. cit.*) have shown that acetylation of systems of the type $>$CH·CO·CH$<$ may give isomeric products.

Attempts to effect the cyclisation of the acetoacetyl-ketones were unsuccessful. With aqueous acids or bases, hydrolysis occurred very readily, whilst with anhydrous catalysts complex condensations took place or the compounds were unaffected. The failure to cyclise may perhaps be accounted for by the fact that these ketones are highly enolised. They were all readily soluble in aqueous alkali, gave intense red colours with ferric chloride, and formed copper complexes.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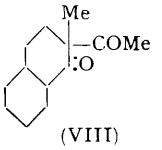
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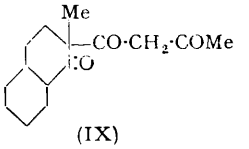
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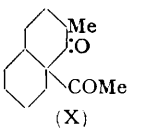
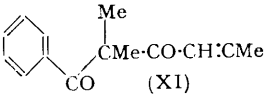

(X)

Crotonic anhydride and *iso*butyrophenone gave α-crotonoyl*iso*butyrophenone (2-benzoyl-2-methylhex-4-en-3-one) (XI), and similarly 2-methyl-*trans*-1-decalone furnished 2-crotonoyl-2-methyl-*trans*-1-decalone (XII). Neither of these products could be cyclised to a six-membered ring-ketone. Oxidation of the ketone (XII) with permanganate gave 2-methyl-1-decalone-2-carboxylic acid (XIII), identical with the acid obtained by Dr. H. Holtermann, in this laboratory, by the carboxylation of 2-methyl-*trans*-1-decalone with sodium triphenylmethyl and carbon dioxide. The position of the crotonoyl side-chain is therefore established.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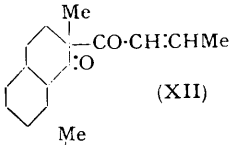
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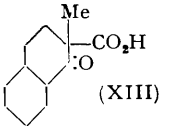
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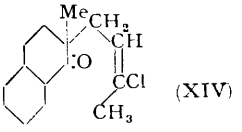
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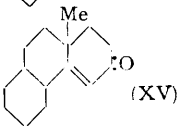
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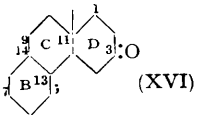
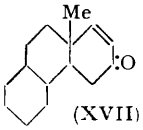

(XVI)

The researches of Wichterle (*Coll. Czech. Chem. Comm.*, 1947, **12**, 93; 1948, **13**, 300) and of Prelog, Barman, and Zimmermann (*Helv. Chim. Acta*, 1949, **32**, 1284) have shown that 1 : 3-dichlorobut-2-ene condenses with enolisable ketones and esters, and the products can be cyclised smoothly. We have found that 2-methyl-*trans*-1-decalone condenses with 1 : 3-dichlorobut-2-ene to give 2-(3-chlorobut-2-enyl)-2-methyl-*trans*-1-decalone (XIV), which cyclised with sulphuric acid to $\Delta^{4(14)}$-dodecahydro-11-methyl-3-oxophenanthrene (XV) (cf. Pinder and Robinson, *J.*, 1952, 1224, for an analogous preparation starting from 1-methyl-*cis*-α-decalone), identical with the product obtained in this laboratory by Dr. H.

Holtermann by condensation of 2-methyl-*trans*-1-decalone with 4-diethylaminobutan-2-one methiodide. Catalytic hydrogenation gave perhydro-11-methyl-3-oxophenanthrene (XVI). The C/D-junction in this compound was almost certainly *cis*, because bromination and dehydrobromination of the saturated ketone (XVI) regenerated the unsaturated ketone (XV), and not the isomeric product (XVII), the intermediate bromo-ketone being 4-bromoperhydro-11-methyl-3-oxophenanthrene (XVIII) (cf. Butenandt and Wolff, *Ber.*, 1935, **68**, 2091).



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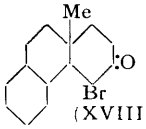

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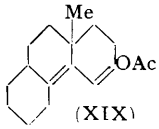

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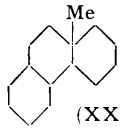
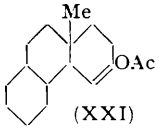
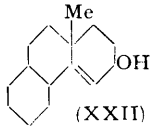


(XX)

Treatment of the enone (XV) with acetyl chloride and acetic anhydride (cf. Inhoffen, *Ber.*, 1936, **69**, 2146) afforded an enol acetate, which because of its ultraviolet absorption spectrum appeared to be 3-acetoxy-$\Delta^{3:12}$-decahydro-11-methylphenanthraene (XIX). Catalytic hydrogenation of the enol acetate using Adams platinum oxide gave perhydro-11-methylphenanthrene (XX), whilst use of palladised strontium carbonate afforded an intermediate enol acetate (XXI) (not isolated), which was converted by hydrolysis into the saturated ketone (XVI), so that the 12 : 13-double bond was reduced in preference to that at the 3 : 4-position.



(XXI)



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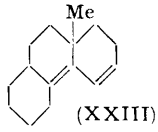

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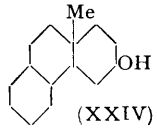


(XXIV)

Reduction of the enone (XV) by Ponndorf's method (cf. Schoenheimer and Evans, *J. Biol. Chem.*, 1936, **114**, 567) gave a mixture of epimerides of $\Delta^{4(12)}$-dodecahydro-3-hydroxy-11-methylphenanthrene (XXII). Dehydration of this alcohol with acid gave $\Delta^{3:12}$-decahydro-11-methylphenanthrene (XXIII), the position of the double bonds being established by the ultraviolet absorption spectrum.

Reduction of the unsaturated ketone (XV) with sodium and *iso*pentyl alcohol gave perhydro-3-hydroxy-11-methylphenanthrene (XXIV) as a mixture of stereoisomerides. Oxidation of this alcohol by means of chromic acid afforded the saturated ketone (XVI), with a *cis*-C/D-configuration.

When an attempt was made to condense the diketone (III) and ethyl acetate with the help of sodium, the triketone (IV) was not produced but, instead, ω-*iso*butyrylacetophenone (4-methyl-1-phenylpentane-1 : 3-dione) (XXV) (Stylo, Beyer, and Claisen, *Ber.*, 1887, **20**, 2181). The same result was obtained without the use of ethyl acetate. The rearrangement of the diketone (III) might be intramolecular or intermolecular, but a third possibility, that of fission and resynthesis, is perhaps the most natural explanation.

If we postulate intramolecular rearrangement, or intermolecular double decomposition, there can be no theoretical difficulty in bringing the new case into line with the usual β-diketone synthesis.

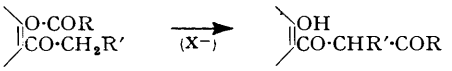
All β-diketones contain bound acyl residues from which the related acids or their derivatives can readily be generated, for example, by hydrolysis, alcoholysis, or aminolysis. The carbonyl groups of these acyl groups are markedly cationoid in electrochemical character and can therefore be attacked by the electron-donating anions of the enols of the keto-methylene groups. Fission will supervene and the net result is the transfer of the acyl group from a certain position to another similar but more stable union.

$CHMe_2 \cdot CO \cdot CH_2 \cdot COPh$ (XXV) $\qquad R \cdot CO \cdot CR'R'' \cdot CO \cdot CH_3 \longrightarrow CHR'R'' \cdot CO \cdot CH_2 \cdot COR$

The closest formal analogy of which we are aware is provided by the annexed transformation of certain esters in the *cyclo*hexanone series (Openshaw and Robinson, *J.*, 1937, 941). This process, however, almost certainly proceeds by ring-opening alcoholysis and Dieckmann-type ring-closure of the resulting substituted pimelic ester. Fission and

recombination is an obvious possibility in the new case but would require the presence of a catalytic quantity of alcohol (sodium ethoxide). Actually a trace of alcohol was added to the ethereal solution, so that this condition was satisfied.

Another analogous process is the internal acylation of ketones established by Baker and by Venkataraman (Baker, *J.*, 1933, 1381; Mahal and Venkataraman, *J.*, 1934, 1767; Nowlan, Slavin, and Wheeler, *J.*, 1950, 340; Gowan and Wheeler, *ibid.*, p. 1925):



Until it is established that the new reaction is intramolecular, or intermolecular, or involves the intervention of another substance such as alcohol leading to fission and recombination, it is unnecessary to speculate about the detailed mechanism. In any case there can be no difficulty in representation of the reaction as essentially a β-diketone synthesis of Claisen type.

Experimental

iso*Butyrophenone*.—The Friedel–Crafts reaction between benzene and *iso*butyryl chloride (Schmidt, *Ber.*, 1889, **22**, 3250) gave phenyl *iso*propyl ketone, b. p. 93—97°/11 mm., in 48% yield. The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate as orange, elongated prisms, m. p. 159° (Found: C, 58·1; H, 4·8. $C_{16}H_{16}O_4N_4$ requires C, 58·5; H, 4·9%).

α-*Acetyl*iso*butyrophenone* (3-*Benzoyl*-3-*methylbutan*-2-*one*) (III).—A mixture of *iso*butyrophenone (20 g.) and acetic anhydride (27·5 g.) was saturated with boron trifluoride at 0° during 1·5 hr., the increase in weight being 19·5 g. The dark syrup was poured into a cold solution of crystallised sodium acetate (45 g.) in water (100 c.c.), and the oil extracted with ether. The ethereal solution was extracted several times with 5% sodium hydroxide solution, dried, and distilled. The residue was distilled *in vacuo* through a 20-cm. lagged Dufton column, giving α-acetyl*iso*butyrophenone, b. p. 125—128°/14 mm. (14 g.) (Found: C, 75·6; H, 7·5. Calc. for $C_{12}H_{14}O_2$: C, 75·8; H, 7·4%). Morton, Hassan, and Calloway (*J.*, 1934, 891) give b. p. 84°/2 mm. The diketone was a pale yellow liquid, insoluble in dilute alkali. It gave no colour with ferric chloride, and formed no copper complex. Hydrolysis by boiling with dilute alkali gave *iso*butyrophenone, methyl *iso*propyl ketone, and acetic and benzoic acid.

The *monoxime* separated from aqueous ethanol in clusters of elongated prisms, m. p. 148° (Found: C, 70·2; H, 7·2. $C_{12}H_{15}O_2N$ requires C, 70·2; H, 7·3%). The *monosemicarbazone* crystallised from ethanol in elongated prisms, m. p. 167—168° (Found: C, 63·2; H, 7·0. $C_{13}H_{17}O_2N_3$ requires C, 63·2; H, 6·9%). The *bis*-2 : 4-*dinitrophenylhydrazone* was dimorphous, one form separating from ethyl acetate in small red prisms, m. p. 136° (Found: C, 52·4; H, 4·1%), and the other in red prisms, m. p. 197—198° (Found: C, 52·2; H, 4·4. $C_{24}H_{22}O_8N_8$ requires C, 52·4; H, 4·0%).

Acidification of the alkaline washings gave an oil which was taken up in ether and washed with sodium hydrogen carbonate. Evaporation of the ethereal solution left an oil (1·0 g.), identified as 5-benzoyl-5-methylhexane-2 : 4-dione (see below).

*Reaction of α-Acetyl*iso*butyrophenone with Sodium*.—A solution of the diketone (7·6 g.) in ether (5 c.c.), containing one drop of alcohol, was added to a suspension of sodium wire (2·0 g.) in dry ether (20 c.c.). The mixture was kept for 24 hr. after which the unchanged sodium was destroyed by addition of a little alcohol, and ice was added. The aqueous layer was extracted twice with ether, then acidified, and the product isolated with ether. After drying and evaporation a yellow oil remained, which distilled at 125—130°(bath)/0·15 mm. (1·5 g.). This diketone was converted into its copper complex, which separated from light petroleum (b. p. 60—80°) in dark green prisms, m. p. 161—162°. Decomposition of the complex with dilute sulphuric acid and ether gave an oil which distilled at 115—120°(bath)/0·2 mm. (1·3 g.) (Found: C, 75·4; H, 7·2. Calc. for $C_{12}H_{14}O_2$: C, 75·8; H, 7·4%).

With 2 : 4-*dinitrophenylhydrazine* the product gave 1-(2 : 4-*dinitrophenyl*)-3-*phenyl*-5-iso*propylpyrazole*, which separated from alcohol as golden-yellow rhombs, m. p. 144° (Found: C, 61·2; H, 4·6; N, 15·9. $C_{18}H_{16}O_4N_4$ requires C, 61·3; H, 4·5; N, 15·9%).

Alkaline hydrolysis of the original product gave benzoic acid, acetophenone, and *iso*butyric acid (anilide, m. p. 105°).

*iso*Butyrylacetophenone (4-methyl-1-phenylpentane-1 : 3-dione), prepared as described by Stylos, Beyer, and Claisen (*Ber.*, 1887, **20**, 2181) from acetophenone and ethyl *iso*butyrate, distilled at 125—130°(bath)/0·2 mm. and gave a copper complex and a pyrazole identical (m. p., mixed m. p., etc.) with the derivatives described above.

5-Benzoyl-5-methylhexane-2 : 4-dione (IV).—A solution of α-acetyl*iso*butyrophenone (9·5 g.) in acetic anhydride (10·2 g.) was saturated with boron trifluoride at 0° during 1 hr. The syrupy product was poured into a solution of sodium acetate (25 g.) in water (50 c.c.), and the oil which separated taken up in ether. The ethereal solution was repeatedly extracted with cold dilute alkali until an extract, after acidification, gave no ferric reaction. The combined alkaline extracts were acidified and the oil was extracted with ether. The ethereal solution was washed with sodium hydrogen carbonate, dried, and distilled. *5-Benzoyl-5-methylhexane-2 : 4-dione* was obtained as a pale yellow oil, b. p. 140—143°(bath)/1 mm. (1·5 g.) (Found : C, 72·5; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). The substance developed a wine-red colour with ferric chloride, and was readily soluble in dilute alkali. Alkaline hydrolysis gave benzoic acid, *iso*butyrophenone, acetone, and methyl *iso*propyl ketone. The copper complex, prepared by shaking an ethereal solution of the triketone with a saturated solution of cupric acetate, separated from a large volume of light petroleum (b. p. 60—80°) in pale blue prisms, m. p. 192°. The *monosemicarbazone* crystallised from ethanol in elongated prisms, m. p. 169—170° (decomp.) (Found : C, 61·9; H, 6·7; N, 14·4. $C_{15}H_{19}O_3N_3$ requires C, 62·3; H, 6·6; N, 14·5%). Attempts to cyclise the triketone were unsuccessful.

α-Crotonoylisobutyrophenone (*2-Benzoyl-2-methylhex-4-en-3-one*) (XI).—A solution of *iso*butyrophenone (5 g.) in crotonic anhydride (10·6 g.; Glover and Richmond, *Amer. Chem. J.*, 1903, **29**, 194) was saturated with boron trifluoride at 0° during 1 hr. The dark syrup was decomposed with a solution of sodium acetate (20 g.) in water (50 c.c.). The product, isolated by means of ether, was fractionated *in vacuo* : *α-crotonoylisobutyrophenone* (4·0 g.) distilled at 125—127°(bath)/0·75 mm. (Found : C, 77·8; H, 7·5. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%). Alkaline hydrolysis afforded *iso*butyrophenone, and benzoic and crotonic acids. The *disemicarbazone* separated from ethanol in elongated prisms, m. p. 265° (decomp.) (Found : C, 58·3; H, 6·5; N, 26·0. $C_{16}H_{22}O_2N_6$ requires C, 58·2; H, 6·7; N, 25·5%). Cyclisation of the diketone could not be effected.

2-Acetyl-2-methyl-indan-1-one (V).—A mixture of 2-methylindan-1-one (Kipping and Clarke, *J.*, 1903, **83**, 915) (7·3 g.) and acetic anhydride (10·2 g.) was saturated with boron trifluoride at 0°. The mixture, worked up in the usual manner, gave on distillation *2-acetyl-2-methylindan-1-one* (4·7 g.), b. p. 135—140°(bath)/0·7 mm. (Found : C, 76·5; H, 6·2. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%). Alkaline hydrolysis gave methylindanone and acetic acid. The *bis-2 : 4-dinitrophenylhydrazone* separated from ethyl acetate as orange-red rhombs, m. p. 143° (decomp.) (Found : C, 53·0; H, 4·3. $C_{24}H_{20}O_8N_8,C_4H_8O_2$ requires C, 52·8; H, 4·4%). The *monosemicarbazone* separated from ethanol in elongated prisms, m.p. 211° (Found : C, 63·3; H, 6·4. $C_{13}H_{15}O_2N_3$ requires C, 63·7; H, 6·1%).

A small quantity of 2-acetoacetyl-2-methylindan-1-one (see below) was also obtained in this reaction.

2-Acetoacetyl-2-methylindan-1-one (VI).—A solution of 2-acetyl-2-methylindan-1-one (18·8 g.) in acetic anhydride (20·4 g.) was saturated with boron trifluoride at 0°. Decomposition of the mixture in the usual manner, followed by extraction with alkali, afforded *2-acetoacetyl-2-methylindan-1-one* (3·0 g.) which distilled at 150°(bath)/0·1 mm. (Found : C, 73·3; H, 6·2. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%). The triketone was readily soluble in dilute alkali and gave a wine-red ferric colour. The copper complex separated from benzene in dark green prisms, m. p. 147—148°. With 6 : 6′-diaminoveratrone, a *copyrine* was obtained (cf. Lawson, Perkin, and Robinson, *J.*, 1924, **125**, 630, 647), which separated from nitrobenzene in dull yellow needles, m. p. >280° (Found : N, 5·4. $C_{31}H_{28}O_5N_2$ requires N, 5·5%).

Attempts to effect an intramolecular cyclisation of the triketone were unsuccessful.

2-Methyl-trans-1-decalone (VII).—The synthesis of this ketone was effected from 1-naphthol by the procedure described by Dr. E. B. J. Smith (D.Phil. Thesis, Oxford, 1949). The *2 : 4-dinitrophenylhydrazone* separated from ethyl acetate in red needles, m. p. 239° (decomp.) (Found : C, 58·8; H, 6·0; N, 15·8. $C_{17}H_{22}O_4N_4$ requires C, 58·9; H, 6·3; N, 16·2%).

The *semicarbazone* crystallised from 60% ethanol in stout prisms, m. p. 221° (Found : C, 64·6; H, 9·4. $C_{12}H_{21}ON_3$ requires C, 64·6; H, 9·4%). The discrepancies in m. p. between these derivatives and those of the 2-methyl-1-decalone described by Cook and Lawrence (*J.*,

1937, 818) are to be ascribed to stereochemical differences; it is probable that the product obtained by these authors was not stereochemically homogeneous.

2-*Acetyl*-2-*methyl*-trans-1-*decalone* (VIII).—A mixture of 2-methyl-*trans*-1-decalone (8·3 g.) and acetic anhydride (10·2 g.) was saturated with boron trifluoride at 0°. The mixture was worked up in the usual manner. Fractional distillation gave 2-acetyl-2-methyl-1-decalone (7·5 g.), b. p. 122—125°(bath)/0·25 mm. (Found : C, 75·7, 75·6; H, 10·0, 13·2. Calc. for $C_{13}H_{20}O_2$: C, 75·0; H, 9·6%). Owing to the difficulty of separating the product completely from unchanged 2-methyl-1-decalone, better analytical figures could not be obtained. Alkaline hydrolysis gave 2-methyl-1-decalone and acetic acid. The *monosemicarbazone* separated from methyl alcohol in minute prisms, m. p. 239—240° (decomp.) (Found : C, 63·5; H, 8·4; N, 15·9. $C_{14}H_{23}O_2N_3$ requires C, 63·4; H, 8·7; N, 15·8%).

2-*Acetoacetyl*-2-*methyl*-1-*decalone* (IX).—Saturation of a mixture of 2-acetyl-2-methyl-1-decalone (7·0 g.) and acetic anhydride (7·0 g.) with boron trifluoride at 0° gave a small yield (0·5 g.) of the alkali-soluble 2-*acetoacetyl*-2-*methyl*-1-*decalone*, b. p. 160°(bath)/0·2 mm. (Found : C, 71·6; H, 8·8. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%). The triketone gave an intense wine-red ferric reaction, and formed a greenish-blue copper complex, which did not crystallise. Attempts to cyclise the triketone were unsuccessful.

2-*Crotonoyl*-2-*methyl*-1-*decalone* (XII).—A mixture of 2-methyl-*trans*-1-decalone (10 g.) and crotonic anhydride (18·6 g.) was saturated with boron trifluoride at 0°, and the mixture decomposed in the usual manner. Isolation of the product with ether and distillation gave 2-*crotonoyl*-2-*methyl*-1-*decalone* (6·2 g.), b. p. 108—110°/0·1 mm. (Found : C, 76·4; H, 9·4. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·4%). Alkaline hydrolysis afforded 2-methyl-*trans*-1-decalone and crotonic acid. Attempts to cyclise the diketone failed. Oxidation with potassium permanganate gave 2-methyl-1-decalone-2-carboxylic acid (XIII), m. p. 117°, alone or when mixed with a specimen obtained by Dr. H. Holtermann by carboxylation of 2-methyl-1-decalone.

1 : 3-*Dichlorobut*-2-*ene*.—The commercial product was washed with sodium hydrogen carbonate, dried ($CaCl_2$), and distilled, giving the pure *trans*-form, b. p. 127—128° (Hatch and Ballin, *J. Amer. Chem. Soc.*, 1949, **71**, 1039).

$\Delta^{4(12)}$-*Dodecahydro*-11-*methyl*-3-*oxophenanthrene* (XV).—2-Methyl-*trans*-1-decalone (5·5 g.) in dry ether (25 c.c.) was added to an ethereal solution of sodium triphenylmethyl (300 c.c. of 0·11M; " Organic Reactions," Vol. I, p. 286), with swirling and cooling under dry nitrogen. After 30 min., 1 : 3-dichlorobut-2-ene (4·2 g.) in ether (25 c.c.) was added, with shaking. After being kept at room temperature overnight, the mixture was refluxed for 4 hr. Water was added to the cooled mixture, and the ethereal layer dried and evaporated. The syrupy residue was triturated with a little methanol and kept at 0° for several hours. The deposit of triphenylmethane was collected and washed with a little cold methanol. Evaporation of the filtrate gave an oil which was fractionated *in vacuo*. 2-(3-Chlorobut-2-enyl)-2-methyl-1-decalone (XIV) distilled at 100—110°/0·08 mm. (4·9 g.). Some unchanged 2-methyl-*trans*-1-decalone was obtained as a fore-run, and triphenylmethane appeared in higher fractions. The product was not further purified.

This chloro-ketone (2·0 g.) and concentrated sulphuric acid (2 c.c.) were carefully mixed with cooling, and kept at the room temperature overnight. Ice was added and the oil which separated taken up in ether. The ethereal solution was washed with sodium hydrogen carbonate solution and water and dried. Evaporation gave a yellow oil (1·3 g.) which was dissolved in light petroleum (b. p. 40—60°) and purified by absorption on an alumina column. Elution with benzene furnished Δ^4-*dodecahydro*-11-*methyl*-3-*oxophenanthrene*, b. p. 140—145°(bath)/ 0·05 mm. (1·1 g.) (Found : C, 82·4; H, 10·3. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%). The ketone was a pale yellow oil, having a strong ultraviolet absorption band at 245 mμ (log ε 3·9). The *semicarbazone* crystallised from methanol in colourless rhombs, m. p. 230·5° (decomp.) (Found : C, 69·7; H, 8·8. $C_{16}H_{25}ON_3$ requires C, 69·8; H, 9·1%); this derivative was sensitive to light, gradually becoming greenish-yellow. It proved to be identical with the semicarbazone obtained by Dr. H. Holtermann (*loc. cit.*) from 2-methyl-*trans*-1-decalone and 4-diethylaminobutan-2-one methiodide. The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in deep red plates, m. p. 208° (Found : C, 62·8; H, 6·4. $C_{21}H_{26}O_4N_4$ requires C, 63·3; H, 6·5%).

Perhydro-11-*methyl*-3-*oxophenanthrene* (XVI).—A solution of the above unsaturated ketone (0·37 g.) in ethanol (8 c.c.) was shaken with a little Adams platinic oxide in an atmosphere of hydrogen at room temperature and pressure. The theoretical absorption for the reduction of one double bond was complete in 1 hr. The *perhydro-ketone* produced distilled at 135—138° (bath)/0·07 mm. (0·35 g.) (Found : C, 81·7; H, 10·7. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9%).

The *semicarbazone* separated from a large volume of methanol in plates, m. p. 231—232° (Found : C, 69·2; H, 9·9. $C_{16}H_{27}ON_3$ requires C, 69·3; H, 9·7%); it was not light-sensitive.

4-Bromoperhydro-11-methyl-3-oxophenanthrene (XVIII).—Perhydro-11-methyl-3-oxophenanthrene (0·5 g.) in carbon tetrachloride (5 c.c.) was heated under reflux on the steam-bath with *N*-bromophthalimide (0·55 g.) for 30 min. The cooled solution was freed from phthalimide by filtration. Evaporation of the filtrate afforded 4-bromoperhydro-11-methyl-3-oxophenanthrene (0·8 g.) as a syrup, which was not purified; free hydrogen bromide was in evidence.

Dehydrobromination by heating the whole crude product in lutidine (20 c.c.) at 170° under reflux gave an unsaturated ketone identical with Δ^1-dodecahydro-11-methyl-3-oxophenanthrene (XVII) (semicarbazone, m. p. 230—230·5°, and 2 : 4-dinitrophenylhydrazone, m. p. 208°, alone or mixed with authentic specimens).

3-Acetoxy-$\Delta^{3:12}$-decahydro-11-methylphenanthrene (XIX).—Δ^4-Dodecahydro-11-methyl-3-oxophenanthrene (0·3 g.), acetic anhydride (3 c.c.), and acetyl chloride (4·5 c.c.) were refluxed for 4 hr., the acetyl chloride being slowly distilled. The mixture was finally refluxed for a further hour, and the solvents were evaporated *in vacuo*. The residual oil was taken up in ether, and the solution washed with sodium hydrogen carbonate and with water, dried, and evaporated. The *enol acetate* distilled at 145—150°(bath)/0·03 mm. (0·3 g.) (Found : Ac, 16·7. $C_{17}H_{24}O_2$ requires Ac, 16·5%). The acetate showed maximum absorption in the ultraviolet region at 240 mμ (log ε 3·7). It gave a yellowish-brown colour with tetranitromethane in chloroform. Acid or alkaline hydrolysis regenerated the original unsaturated ketone.

Perhydro-11-methylphenanthrene (XX).—The above enol acetate (0·5 g.) in ethanol (8 c.c.) was shaken with Adams platinum oxide in an atmosphere of hydrogen at the room temperature and pressure. After 2 hr., reduction was complete, 3 mols. being absorbed. The solution, now strongly acid, was filtered and the filtrate evaporated *in vacuo*. The residue, *perhydro-11-methylphenanthrene*, distilled at 110—115°(bath)/0·05 mm. (0·35 g.) (Found : C, 87·3; H, 12·8. $C_{15}H_{26}$ requires C, 87·4; H, 12·6%). The product had a pleasant terpenoid odour, and there was no colouration with tetranitromethane.

Reduction of the enol acetate (0·4 g.) in ethanol (8 c.c.) in the presence of palladised strontium carbonate caused the absorption of hydrogen equivalent to H_2. The product (XXI) was hydrolysed by 7 hours' refluxing with aqueous 5N-potassium hydroxide (10 c.c.) and methanol (10 c.c.). Evaporation of the methanol and ether-extraction afforded Δ^4-dodecahydro-11-methyl-3-oxophenathrene, identical with an authentic specimen.

Δ^4-Dodecahydro-3-hydroxy-11-methylphenanthrene (XXII).—The Δ^4-ketone (1·0 g.) was added to a solution of aluminium *iso*propoxide (4 g.) in dry *iso*propyl alcohol (25 c.c.), and the mixture heated on the steam-bath, under an Allihn partial condenser, so that distillation occurred at the rate of about one drop every 5 sec. The distillate gave a negative Lund test for acetone after 1 hr. A further 10 c.c. of *iso*propyl alcohol was added and the mixture refluxed for 30 min., and then distilled for a further 30 min. Decomposition with ice and potassium hydroxide solution (20 c.c. of 20%) and ether-extraction gave the alcohol (1·0 g.) as a mixture of epimerides (cf. Schoenheimer and Evans, *J. Biol. Chem.*, **1936**, **114**, 587).

$\Delta^{3:12}$-Decahydro-11-methylphenanthrene (XXIII).—A solution of the above epimeric alcohols (1·0 g.) in 95% ethanol (25 c.c.) containing two drops of concentrated hydrochloric acid was gently refluxed for 4 hr. The cooled solution was poured into a large volume of water, and the product isolated with ether. The *diene* distilled at 105°(bath)/0·08 mm. (0·7 g.) (Found : C, 88·8; H, 11·0. $C_{15}H_{22}$ requires C, 89·1; H, 10·9%). The product gave a brownish-yellow colour with tetranitromethane in chloroform, and showed maximum absorption in the ultraviolet region at 245 mμ (log ε 4·1).

Perhydro-3-hydroxy-11-methylphenanthrene (XXIV).—Sodium (4·0 g.) was added in small pieces to a gently refluxing solution of the Δ^4-ketone (0·5 g.) in dry pentyl alcohol (30 c.c.) during 1 hr. The solution was finally refluxed at 210—215° for 3½ hr. Ice was added, followed by water and ether. The ethereal layer was separated, dried, and evaporated. *Perhydro-3-hydroxy-11-methylphenanthrene* distilled at 140—145°(bath)/0·04 mm. (0·5 g.) (Found : C, 81·0; H, 11·5. $C_{15}H_{26}O$ requires C, 81·1; H, 11·7%). Oxidation of the product (0·5 g.) in acetic acid (8 c.c.) with chromic acid (0·25 g.) gave *perhydro-11-methyl-3-oxophenanthrene* (semicarbazone, m. p. and mixed m. p. 232°).

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