135. *Fused Carbon Rings. Part XIX. Experiments on the Synthesis of Tetracyclic Compounds of the Sexual Hormone Type*

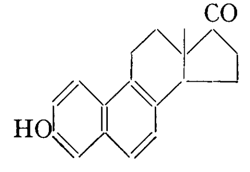
By V. C. E. Burnop, G. H. Elliott, and R. P. Linstead.

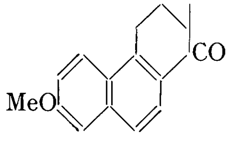
The experiments were directed towards the synthesis of equilenin and similar compounds. The preparation of the key-intermediate, 1-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, has been improved. Its condensation with Δ^{δ}-pentenylmagnesium bromide, followed by permanganate oxidation and cyclisation with phosphoric oxide, yielded a tetracyclic ketone, probably the ketomethoxymethylhexahydrochrysene (VIII), from which a number of derivatives were prepared. The preparation and cyclisation of 2-methyl-1-Δ^{γ}-butenyl-3 : 4-dihydrophenanthrene has been further studied. This diene is conveniently obtained pure by regeneration from its trinitrobenzene compound. It yields 2-methyl-1-butylphenanthrene by rearrangement over palladium. It is best cyclised to 16-methylhexahydrochrysene by phosphoric oxide at 140°. The tetracyclic hydrocarbon so obtained resists degradation of ring *D*.

The methods for the conversion of 2-methyl*cyclo*hexanone into 8-methyl-1-hydrindanone (Elliott and Linstead, J., 1938, 660; Burnop and Linstead, preceding paper) have been applied to the analogous synthesis of equilenin (I) from 1-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (II). Although we have been able to prepare tetracyclic material, the main objective has not yet been realised. We are led to present this incomplete account of our experiments by the appearance of a preliminary report by Bachmann, Cole, and Wilds describing an elegant synthesis of equilenin (*J. Amer. Chem.*

Soc., 1939, **61**, 974),* and because the collaboration of the present authors has come to an end.

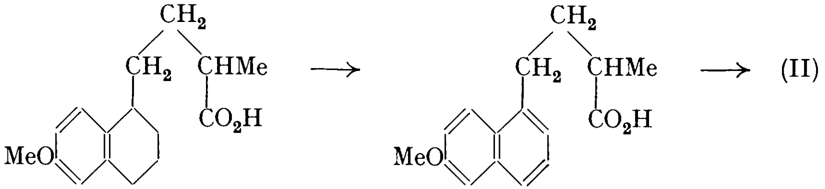
(I.)





(II.)

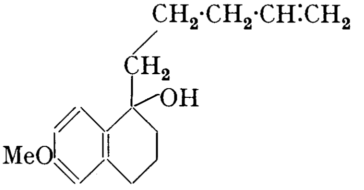
The tricyclic ketone (II) has been prepared essentially by Haberland and Blanke's method (*Ber.*, 1937, **70**, 169), which has been improved in several respects. The overall yield of the ketone in the 12-stage synthesis from sodium tetralin-β-sulphonate is 10%. The dehydrogenation of α-methyl-γ-(6-methoxy-1-tetralyl)butyric acid (III) to the corresponding naphthalene derivative (IV) was conveniently effected by palladium. The cyclisation of (IV) by means of phosphoric oxide in benzene gave an excellent yield of the tricyclic ketone (II) without side reaction. For some experiments on the formation of the fourth ring, we have used the corresponding unmethoxylated 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene of Cohen, Cook, and Hewett (J., 1935, 1633), which is more accessible.

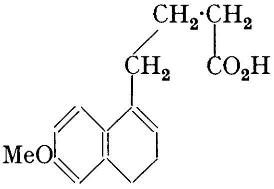


(III.) (IV.)

Before applying the " pentenyl " method of Elliott and Linstead (*loc. cit.*) to a tricyclic ketone, the reaction between Δ^{δ}-*n*-pentenylmagnesium bromide and 6-methoxy-1-tetralone was studied in order to determine whether the conjugation of the carbonyl group with an aromatic ring had any deleterious effect on the process. The condensation readily yielded 6-*methoxy*-1-Δ^{δ}-*pentenyl*-1-*tetralol* (V). The alcohol was oxidised with potassium permanganate, and the product dehydrated with oxalic acid and freed from lactone. In this way a solid acid, mainly γ-6-methoxy-3 : 4-dihydro-1-naphthylbutyric acid (VI), was obtained.

(V.)





(VI.)

This acid has been prepared by a different method by Robinson and Walker (J., 1937, 60). Our product resembled theirs and had an unsharp melting point.

The Grignard reagent prepared from Δ^{δ}-pentenyl bromide reacted readily with the tricyclic ketone (II). The alcoholic product was oxidised with permanganate and the acid so formed (VII) was cyclised by means of phosphoric oxide in boiling benzene.† The crystalline tetracyclic *ketone*, $C_{20}H_{20}O_2$, isolated from the product readily absorbed hydrogen over Adams's catalyst. If the hydrogenation were stopped when 1 mol. had been taken up, the product was a saturated *ketone*, $C_{20}H_{22}O_2$. If it were allowed to go to completion, rather more than 2 mols. of hydrogen were absorbed and a saturated alcohol was formed.

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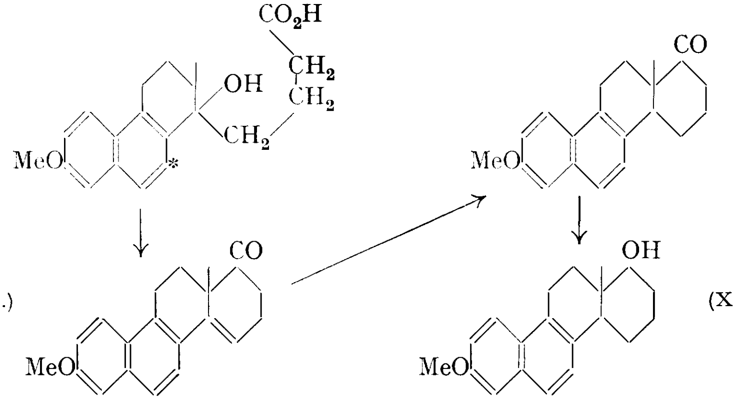
* Since this paper was written, a full report by these authors has appeared (*J. Amer. Chem. Soc.*, 1940, **62**, 824).

† A method which Mr. R. S. Hughes of this College has found very satisfactory for cyclisations of this type, for example, of γ-(2-methyl-Δ^1-*cyclo*hexenyl)butyric acid to 9-methyl-1-octalone.

This was isolated as the crystalline *trinitrobenzene* addition compound. These substances are probably the methoxymethylhexahydrochrysene derivatives shown below:

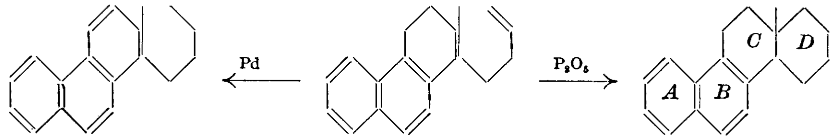


(VII.) (VIII.) (IX.) (X.)

These structures are favoured by analogy with the formation of 9-methyloctalone by a similar cyclisation; and because Cohen, Cook, and Hewett (J., 1935, 1633) have shown that 2-methyl-1-butenyldihydrophenanthrene can be cyclised to a hydrochrysene derivative of similar skeleton. Additional evidence on this point is given later in the present paper. The possibility cannot be quite excluded that the products contain a seven-membered ring formed by cyclisation on to the *peri*-carbon atom, asterisked in formula (VII) (cf. Kon and Soper, J., 1939, 790; Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 4347). We have not yet obtained any evidence capable of settling this point. Experiments on the oxidation of the tetracyclic compounds to dibasic acids by the methods successful in the dicyclic series have been fruitless.

The next series of experiments was concerned with the cyclisation of 2-methyl-1-Δ^{γ}-butenyldihydrophenanthrene (XI), already studied by Cohen, Cook, and Hewett (*loc. cit.*), who were unable to isolate any homogeneous compounds from the product but established the closure of the fourth ring by dehydrogenation to chrysene. We were encouraged to reopen this subject by the results of our reinvestigation of the dehydration of 9-methyl-2-decalol (preceding paper). As observed by the previous investigators the diene (XI) is not easily obtained pure. The product from the Grignard reaction was best dehydrated by silica gel at 200°, and the diene purified by chromatographic adsorption and through the s-*trinitrobenzene* addition compound. The latter is phototropic, separating in a bright vermilion form which, on exposure to light, changes to an orange-brown. The pure *diene* (XI) was conveniently regenerated (from the red derivative) by treatment with petrol and filtration through alumina (cf. St. Pfau and Plattner, *Helv. Chim. Acta*, 1937, **20**, 224). The structure of the diene was shown by the fact that it readily absorbed 2 mols. of hydrogen over Adams's catalyst, and that it was quantitatively isomerised over palladised charcoal at 260° to 2-*methyl*-1-n-*butylphenanthrene* (XII). The phenanthrene derivative differed from the isomeric diene in being a well-crystallised solid and in giving a very stable *picrate* and *trinitrobenzene* compound. Similar isomerisations of allyl compounds have been observed by Cohen, Cook, and Hewett (*loc. cit.*) and by Bachmann and Wilds (*J. Amer. Chem. Soc.*, 1938, **60**, 624).

Treatment of 2-methyl-1-Δ^{γ}-butenyldihydrophenanthrene (XI) with the acetic–sulphuric acid reagent of Linstead, Millidge, and Walpole (J., 1937, 1140) gave no useful results. No tetracyclic acetate was isolated and the recovery of hydrocarbon was poor, owing to oxidation and, probably, sulphonation. The use of phosphoric acid in place of sulphuric acid was examined. This was first shown to be successful in converting 2-methyl-1-Δ^{γ}-butenyl*cyclo*hexanol into *cis*-9-methyl-2-decalol. The dicyclic alcohol was obtained in rather lower yield than that given by sulphuric acid, but the purity was satisfactory. A temperature of 85° was necessary. When the tricyclic diene (XI) was treated in the same way, the greater part was recovered unchanged but a small amount of tetracyclic material was formed. This was 16-methylhexahydrochrysene (XIII) and not an acetate. It yielded a yellow *trinitrobenzene* compound, m. p. 123°. When the diene was heated to 140° with phosphoric oxide, the yield of this tetracyclic hydrocarbon was greater and a little methylbutylphenanthrene was formed by rearrangement. The tetracyclic hydrocarbon could be regenerated from the trinitrobenzene compound, m. p. 123°, by filtering a petroleum solution through an alumina column. It was shown to be a methylhexahydrochrysene by dehydrogenation with selenium, which yielded chrysene. The position of the double bond is unknown, but it is probably Δ^2- (XIII).



(XII.) (XI.) (XIII.)

Trinitrobenzene compounds. Canary-yellow, m. p. 148°. Orange-red, m. p. 66°. Pale yellow, m. p. 123°.

The next stage was to degrade ring *D* of the tetracyclic hydrocarbon to a five-membered ring containing the carbonyl group, following the methods successful in the dicyclic series. However, all attempts at oxidation failed to give definite products.

In making these experiments on the synthesis of the hormone, we were aware of the stereochemical difficulty that the synthesis would be likely to lead to material with rings *C* and *D* (sterol lettering) locked in the *cis*-position, whereas the natural configuration is probably the reverse of this. Peak's contention (*Nature*, 1937, **140**, 280) that the *C/D* locking in the natural steroids is *cis*- appears unlikely. The evidence from the hydrogenation of ergosterol seems to us to have little weight when assessed against that brought forward by Wieland and his collaborators (see particularly *Z. physiol. Chem.*, 1933, **216**, 91; cf. A. H. Cook and Linstead, J., 1934, 951). Peak suggests that the possibility of an inversion of configuration during the degradation of 12-ketocholanic and deoxycholic acids cannot be excluded. It seems to us that such an inversion is extremely unlikely in the case of deoxycholic acid and that, in the absence of fresh evidence (which would be most desirable), the locking of *C/D* is still to be regarded as *trans*-. Bachmann's synthesis of equilenin, although providing welcome direct evidence as to the location of the angular methyl group on C_{14}, does not appear to clarify the stereochemical problem.

EXPERIMENTAL.*

1. *Preparation of 1-Keto-7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene* (II).—For the early stages of this synthesis, Haberland refers to a dissertation by A. Goertz (Berlin 1924). This information being comparatively inaccessible, we describe our results in detail below.

6-*Methoxytetralin*. Schroeter's method (*Annalen*, 1922, **426**, 119) was modified as follows. In a large iron pan fitted with a mechanical stirrer of wrought iron, a thermometer well and lid, 900 g. of potassium hydroxide were heated to 200—210°. Sodium tetralin-6-sulphonate was then stirred in, 50 g. at a time. Each batch was fused before a fresh addition, and a little more alkali was added at intervals. The melt finally contained 600 g. of the sulphonate and 1200 g. of potassium hydroxide. The temperature, which had been raised to 240° to maintain the mass fluid was finally raised to 280° and maintained for 2¼ hours. The melt was poured into iron trays and broken up while hot. The product was dissolved in 2 l. of water, cooled in ice, and acidified with 50% sulphuric acid. The *ac*-β-tetralol, isolated by means of ether, was dissolved in 1500 c.c. of 10% aqueous sodium hydroxide and methylated with 300 c.c. of methyl sulphate, added in drops with vigorous stirring. The product, isolated by means of ether, yielded 270 g. (65%) of 6-methoxytetralin, b. p. 134—138°/18 mm., and a little 2-methoxynaphthalene, m. p. 72°, as a higher-boiling fraction.

6-*Methoxy*-1-*tetralone*. Chromic acid (140 g.) in water (60 c.c.) and acetic acid (400 c.c.) was added with stirring at 5—10° to 143 g. of 6-methoxytetralin dissolved in 800 c.c. of acetic acid. The addition lasted 5 hours and the mixture was left overnight. The acetic acid was removed,

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* We are greatly indebted to Mr. R. S. Hughes for his assistance in the preparation of the tricyclic ketones used in this work.

water added, and the product distilled in superheated steam (220°). Although this process was tedious—about 40 l. of water and 20 hours' distillation were necessary—it was far preferable to direct extraction with petroleum for the isolation of the pure ketone. The steam distillate was extracted with ether, and the extract washed with aqueous potassium carbonate and dried. Distillation yielded 110 g. (70%) of 6-methoxy-1-tetralone as an oil, b. p. 162—164°/18 mm., which at once solidified and melted at 77·5° after crystallisation from benzene–petrol.

Reformatsky reaction. A mixture of 6-methoxy-1-tetralone (108 g.), ethyl bromoacetate (125 g.), zinc wool (50 g.), and benzene (400 c.c.) was refluxed until reaction started; boiling was continued for 2 hours in all. The product, isolated in the usual way, gave 92 g. (76%) of the hydroxy-ester, b. p. 168—172°/1 mm. Dehydration of this with thionyl chloride and pyridine gave only a 55% yield of an impure unsaturated ester, and potassium hydrogen sulphate also was unsatisfactory. A mechanically stirred mixture of 92 g. of the hydroxy-ester, 300 c.c. of benzene, and 65 g. of phosphoric oxide was refluxed for 3 hours. The product was poured on ice, and the benzene solution washed with aqueous potassium carbonate and water and dried over calcium chloride. Distillation gave an almost theoretical yield of 6-methoxy-3 : 4-dihydro-1-naphthylacetic ester (85 g., b. p. 164—168°/1·5 mm.).

β-(6-*Methoxy*-1-*tetralyl*)*ethyl alcohol and bromide.* The unsaturated ester was reduced by the Bouveault–Blanc procedure, following Haberland (*loc. cit.*). The saturated alcohol was obtained in 72% yield, b. p. 158—162°/1 mm., $d_{4^\circ}^{20^\circ}$ 1·085. A minor amount of hydrolysis (accompanied by reduction) occurred, to give 6-methoxytetralin-1-acetic acid (19%; m. p. 87°, in agreement with Haberland). The acid from several such reductions was esterified, and the saturated ester reduced to the same saturated alcohol. Haberland prepared the bromide by treating the alcohol with phosphorus tribromide in chloroform. Our optimum yield by this process was 58% and one batch polymerised completely to a jelly. A more certain method is the following: A solution of 48 g. of phosphorus tribromide in 75 c.c. of dry benzene was added in drops during 6 hours to a stirred solution of 72 g. of the alcohol and 5 g. of dry pyridine in 200 c.c. of dry benzene. The product was poured on ice and washed with alkali and water. The yield of bromide from two such experiments was 155 g. (82%), b. p. 150—155°/0·7 mm., $d_{4^\circ}^{21^\circ}$ 1·207.

For the next three stages we found the following methods better than those used by Haberland and Blanke (*loc. cit.*). 100 G. of methylmalonic ester in 60 c.c. of xylene were added to 21 g. of " molecular " potassium in 60 c.c. of xylene. After the first vigorous reaction had moderated, the mixture was refluxed at 145° for a few minutes, cooled to 60°, and treated with 155 g. of methoxytetralylethyl bromide in 60 c.c. of xylene. The mixture was boiled for 20 hours (bath at 150°). The ester, isolated in the usual way, was freed from low-boiling products by distillation up to 130°/10 mm. The residue was hydrolysed by methanolic potassium hydroxide (400 c.c. of 20%), and the acid isolated by means of ether. 120 G. (68%) of α-carboxy-α-methyl-γ-6-methoxy-1-tetralylbutyric acid were isolated, m. p. 132° after crystallisation from 75% acetic acid (Haberland and Blanke give m. p. 132—133°). The acid (9·8 g.) was decarboxylated by heating at 165°/40 mm. for 1 hour. 1 G. of 30% palladised asbestos was then added, and the mixture heated at 270—280°/40 mm. for 5 hours. The dehydrogenated product was cooled, and the organic material extracted with acetone. The α-methyl-γ-(6-methoxy-1-naphthyl)butyric acid (IV) was freed from a little neutral gum and solidified immediately. Yield, 7·3 g. (82%). It formed plates from 70% acetic acid, m. p. 87° (Haberland and Blanke, 89°) (Found: C, 74·8, 74·6; H, 6·9, 7·1. Calc. for $C_{10}H_{18}O_3$: C, 74·4; H, 7·0%).

Platinised charcoal also was used for this dehydrogenation. It gave a rather higher proportion of neutral material. The cyclisation of the acid was best effected by phosphoric oxide.* A solution of 52 g. of the dehydrogenated acid in 300 c.c. of dry benzene was freed from traces of water by concentration to 250 c.c. 52 G. of phosphoric oxide were then added and the mixture was refluxed with mechanical stirring for 3 hours. The benzene solution was decanted; the residue was washed once with benzene and then warmed with water, and the solution extracted with ether. The residue from the ethereal extract was added to the benzene solution. This was freed from acid by extraction with 10% alkali solution, dried, and freed from solvent. 1-Keto-7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (II) remained as a crystalline mass, m. p. 107° after crystallisation from light petroleum (b. p. 60—80°). Yield, 41 g. (86%).

2. *Preparation of* 1-*Keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene.*—This was carried out by Cohen, Cook, and Hewett's modification (*loc. cit.*) of Haworth's method (J., 1932, 1125), except that the final cyclisation was effected by the use of stannic chloride as follows: The γ-1-naphthyl-α-methylbutyric acid obtained by decarboxylating 85 g. of the corresponding

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* The action of stannic chloride on the acid chloride was also fairly satisfactory.

malonic acid was dissolved in 300 c.c. of dry ether. After the addition of 24 g. of dry pyridine, 42 g. of thionyl chloride were added during 1 hour with mechanical stirring and ice-cooling. The product was left overnight and filtered. The filtrate and washings were freed from ether and excess of reagents, and the residue was dissolved in 150 c.c. of carbon disulphide. The solution was added at $-15°$ to a stirred mixture of 85 g. of stannic chloride and 150 c.c. of carbon disulphide. After 2 hours at $-15°$, the mixture was allowed to warm to room temperature, and was decomposed by hydrochloric acid (1 : 1) with vigorous stirring. The product was washed with dilute acid and alkali, dried over potassium carbonate, and freed from solvent. The residue (62 g., 95% yield) solidified immediately. The ketone crystallised from light petroleum in large prisms, m. p. 75—76°, in agreement with Haworth.

3. *Condensation of* Δ^δ*-Pentenyl Bromide and* 6-*Methoxy*-1-*tetralone*.—A solution of 6-methoxy-1-tetralone (51 g.) in ether (300 c.c.) and benzene (50 c.c.) was added in drops to the Grignard reagent prepared from 50 g. of Δ^δ-pentenyl bromide (Gaubert, Linstead, and Rydon, J., 1937, 1971) and 8·4 g. of magnesium in ether (300 c.c.). The product was refluxed for an hour, decomposed with aqueous ammonium chloride, washed with sodium thiosulphate solution, and dried. Distillation yielded 6-*methoxy*-1-Δ^δ-*pentenyl*-1-*tetralol* as a viscous liquid (38 g.), b. p. 168—172°/1·5 mm. (Found: C, 78·1; H, 8·5. $C_{16}H_{22}O_2$ requires C, 78·0; H, 9·0%). The alcohol (37·5 g.), suspended in water (50 c.c.), was treated at 0° during 3 hours with 920 c.c. of 1·5% aqueous potassium permanganate containing 6 g. of sodium carbonate. 920 C.c. of 3% permanganate solution containing 12 g. of sodium carbonate were then added during 5 hours at room temperature. The colourless solution was filtered from manganese mud, evaporated to 300 c.c., and freed from neutral material by means of ether. Acidification and further ether extraction then removed the acidic product, which was dried, freed from solvent, and distilled with 5 g. of anhydrous oxalic acid. The thick oil (b. p. 210—220°/2 mm.) was separated into a neutral (6 g.) and an acid (5 g.) fraction. The latter solidified rapidly. Crystallisation from 75% acetic acid gave pale yellow crystals, m. p. 133—134° after softening at 127°. The acid in sodium bicarbonate solution immediately decolourised permanganate (Found: C, 73·1; H, 6·6. Calc. for $C_{15}H_{18}O_3$: C, 73·15; H, 7·3%). Robinson and Walker (*loc. cit.*) describe γ-6-methoxy-3 : 4-dihydro-1-naphthylbutyric acid as softening from 123°, collapsing at 129—130° and clearing at *ca.* 146°. The low hydrogen figure for our acid may indicate a partial dehydrogenation.

4. *Formation of Tetracyclic Compounds from* 1-*Keto*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II).—The Grignard compound prepared from 35 g. of Δ^δ-pentenyl bromide and 6 g. of magnesium was treated with 36 g. of the ketone (II) dissolved in 600 c.c. of ether (in which it was sparingly soluble). The mixture was refluxed for an hour and kept overnight. An oil (42 g.) was recovered. From 10 g. of this, Girard's reagent T removed only 0·5 g. of unreacted solid ketone. Hence the reaction had gone nearly to completion. Chromatographic analysis removed a little colour but led to no separation of solid products. Distillation as a method of purification was impossible owing to the certainty of the introduction of an undesired double bond. 30 G. of the crude product were accordingly dissolved in acetone (100 c.c.) stirred with 6 g. of anhydrous sodium carbonate, and oxidised with 20 g. of potassium permanganate, dissolved in acetone and added during 2 days. The liquid was filtered, the mud washed with hot water, and the solution freed from acetone. Neutral material (17 g.) was removed with ether, and the aqueous solution acidified and extracted with ether. More acid was recovered by dissolving the manganese mud in sulphurous acid and extracting the solution with ether. The ethereal extracts were shaken with water, dried over sodium sulphate, and freed from solvent, finally under reduced pressure. The neutral material was reoxidised and a total yield of 25·5 g. of the acid (VII) was obtained as a partly crystalline gum. Owing to its probable instability, no attempt was made to purify it. 10·5 G. were dissolved in 50 c.c. of dry benzene, and 12 g. of phosphoric oxide added. The mixture was refluxed with vigorous stirring for 3 hours. The benzene solution was decanted, and the black residue decomposed with water and extracted with ether. Acidic material (2·1 g.) was removed from the united solutions by means of alkali and a semi-solid residue of neutral product (5·7 g.) was obtained. A second preparation from 17 g. of the acid yielded 9·5 g. of neutral material and 3 g. of unchanged acid. The united neutral product gave a deep red solution in hot acetone, which deposited a crystalline solid on standing in a refrigerator. After repeated crystallisation from acetone and alcohol, 5·0 g. of the *ketomethoxymethylhexahydrochrysene* (VIII) were obtained, m. p. 185—187°. Most of the red colour associated with the crude material could be removed by charcoal, but the last traces were not removed by this or by chromatographic adsorption, and the material was analysed in the form of pale pink, flattened needles, m. p. 187° (Found: C, 82·4; H, 6·9.

$C_{20}H_{20}O_2$ requires C, 82·1; H, 6·85%). The ketone was soluble in acetone and benzene, less so in the simple alcohols. It gave a white semicarbazone, m. p. 260°.

1·00 G. of the ketone was hydrogenated in 70 c.c. of glacial acetic acid over Adams's catalyst (0·1 g.). The reaction was stopped when 77 c.c. of hydrogen (N.T.P.) had been absorbed. This corresponds to the saturation of one double bond. The solution was filtered, and the acetic acid removed under reduced pressure. Crystallisation of the residue gave 0·6 g. of *ketomethoxymethyloctahydrochrysene* (IX), m. p. 212—213° (Found : C, 81·7; H, 7·3. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%). The semicarbazone melted at 245°.

When the hydrogenation of the unsaturated ketone (600 mg.) was allowed to go to completion under the same conditions, 106 c.c. of hydrogen, corresponding to 2·3 mols., were taken up. The product was a gum. It formed no semicarbazone, but 100 mg. of it with 80 mg. of *s*-trinitrobenzene yielded 170 mg. of an orange-red addition *compound*. This formed needles from methanol, m. p. 155° (Found for a sample dried in a vacuum at 60° : C, 60·2, 60·2; H, 6·0, 5·9. $C_{27}H_{31}O_9N_3$ requires C, 59·9, H, 5·8%). This corresponds to the trinitrobenzene compound of the saturated alcohol (X), containing a molecule of methanol of crystallisation.

5. *Formation of Tetracyclic Compounds from* 1-*Keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (cf. Cohen, Cook, and Hewett, *loc. cit.*).—A solution of 34·0 g. of 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene in 150 c.c. of ether was added slowly to an ice-cold Grignard solution prepared from 48 g. of Δ^{γ}-butenyl bromide and 10 g. of activated magnesium in 200 c.c. of ether. The mixture was boiled for an hour and decomposed with ammonium chloride solution. The dried product was distilled at 1·5 mm.; dehydration then occurred and the bulk boiled at 178°. After a further distillation 31·4 g. were obtained, b. p. about 172°/0·5 mm. This was unsaturated to bromine and permanganate, but gave a ketone reaction with 2 : 4-dinitrophenylhydrazine. A solution of 16 g. in 50 c.c. of light petroleum was run through a column of Merck's alumina. Two bands were produced which gave a blue fluorescence when irradiated with ultra-violet light. The bands were developed by elution with the same solvent. The large lower band was separated, and the alumina extracted with alcohol. The extract from two such adsorptions was diluted with 300 c.c. of benzene, washed with a large bulk of water, dried, and freed from solvent. Distillation then gave 22·2 g., b. p. 159—164°/0·3 mm. (A), together with 7·0 g. of a low fraction. Neither fraction contained ketone. Analysis of the main fraction indicated that it was composed of a mixture of the diene (XI) and some 20% of the corresponding tertiary alcohol (Found : C, 90·35; H, 8·1. Calc. for a mixture of 80% of $C_{19}H_{20}$ and 20% of $C_{19}H_{22}O$: C, 90·65; H, 8·1%). The extent of dehydration in these distillations was variable and in a later experiment we obtained a higher-boiling and more viscous product (B) which contained more of the alcohol (Found : C, 87·9, 87·6; H, 7·8, 7·9%).

920 Mg. of fraction (A) on treatment with 850 mg. of trinitrobenzene in alcohol yielded 1·55 g. of the *trinitrobenzene* addition product of 2-methyl-1-Δ^{γ}-butenyl-3 : 4-dihydrophenanthrene (XI). The compound formed needles, orange-yellow when viewed as single crystals by transmitted light under a microscope, but vermilion in mass; m. p. 65—66° (Found : C, 65·0; H, 5·0. $C_{19}H_{20},C_6H_3O_6N_3$ requires C, 65·0; H, 5·0%). The dehydration of fraction (B) was completed by heating it at 180°/10 mm. with an equal weight of silica gel (first dehydrated at 300°/0·2 mm.). The residue was distilled twice, the second time over 10% of fresh silica gel. This gave an 80% yield of hydrocarbon, b. p. 170°/0·8 mm., which gave an excellent yield of the trinitrobenzene compound described above.

When the trinitrobenzene compound, m. p. 65—66°, was exposed to air and light, the m. p. fell to 60—62° in 2 days and rose to 80—85° after 8 days. The colour changed from vermilion to a dull brownish-yellow. This change does not apparently involve dissociation of the complex, as no liquid separates, or rearrangement to the isomeric derivative of methylbutylphenanthrene, for this melts at 147—148°. It will be examined further.

The freshly prepared derivative is easily dissociated by light petroleum (b. p. 60—80°), which dissolves the hydrocarbon and leaves trinitrobenzene. The regeneration is conveniently completed by filtration through an alumina column; all the trinitrobenzene is then retained and the 2-*methyl*-1-Δ^{γ}-*butenyl*-3 : 4-*dihydrophenanthrene* (XI) can be washed through with light petroleum. It is a colourless oil, b. p. 162°/0·3 mm. (Found : C, 92·2; H, 7·9. $C_{19}H_{20}$ requires C, 91·9; H, 8·1%). The picrate, formed from the regenerated hydrocarbon, was obtained in small, dark red needles, m. p. 72—73° (Found : C, 62·9, 62·9; H, 4·6, 4·8. Calc. for $C_{19}H_{20},C_6H_3O_7N_3$: C, 62·9; H, 4·9%). Cohen, Cook, and Hewett (*loc. cit.*) obtained a dark red picrate, m. p. 77—78°.

On catalytic hydrogenation of the diene (Adams's catalyst, acetic acid) hydrogen corresponding to the saturation of one double bond was absorbed in ½ hour; the second double bond was saturated in 2½ hours. The total hydrogen absorbed was 98·1% of the theoretical.

1·52 G. of the regenerated diene were heated with 0·11 g. of 30% palladised charcoal at 260—265° for 2 hours and at 280—285° for 1 hour. The product, isolated by means of ether, readily solidified. *2-Methyl-*1-n-*butylphenanthrene* (XII) crystallised from methanol in white plates, m. p. 73°, and was saturated to permanganate in moist acetone (Found: C, 92·1; H, 7·85. $C_{19}H_{20}$ requires C, 91·9; H, 8·1%). The s-*trinitrobenzene* addition compound crystallised from alcohol in canary-yellow needles, m. p. 147—148°, and was stable to light petroleum (Found: C, 64·7, 64·9; H, 4·7, 4·7. $C_{19}H_{20},C_6H_3O_6N_3$ requires C, 65·0; H, 5·0%). The *picrate*, which was much less soluble in alcohol than its butenyl isomeride, formed fine orange-yellow needles from that solvent, m. p. 128° (Found: C, 62·95, 63·0; H, 4·6, 4·6. $C_{19}H_{20},C_6H_3O_7N_3$ requires C, 62·9; H, 4·9%).

15 G. of the diene (XI) were treated at 0° with a mixture of 80 c.c. of glacial acetic acid, 11·5 c.c. of acetic anhydride, and 8 c.c. of concentrated sulphuric acid. After 5 days at room temperature the product was poured into water, neutralised with alkali (which removed a considerable quantity of acidic tar) and extracted with benzene. The residue from the benzene was boiled with methanolic potash, and the neutral product extracted with benzene and distilled. There were isolated 3·1 g., b. p. *ca.* 152°/0·5 mm., and 0·9 g. of a high-boiling fraction, which yielded no solid products.

Use of Phosphoric and Acetic Acids.—Various model experiments were carried out on 2-methyl-1-Δ^{γ}-butenyl*cyclo*hexanol (Hibbit, Linstead, and Millidge, J., 1936, 470), of which the following is typical: 24 C.c. of syrupy phosphoric acid (containing 37·5 g. of orthophosphoric acid) were dehydrated at 235° for 1 hour. The product was cooled under a drying tube, diluted with 200 c.c. of glacial acetic acid, and added at 0° to 15 g. of the alcohol. The mixture was kept for 30 hours at room temperature and for 20 hours at 85°; it had then become almost homogeneous. It was cooled, poured on ice, nearly neutralised with alkali, and extracted with ether. The extract on distillation yielded 5·5 g. (38%) of hydrocarbon, b. p. 76—81°/9 mm., and 8·0 g. (38%) of 9-methyldecalyl acetate, b. p. 125—131°/9 mm. Hydrolysis of the second fraction yielded 5·9 g. of *cis*-9-methyl-2-decalol, identical with that of Linstead, Millidge, and Walpole (*loc. cit.*), which was further identified by oxidation to the corresponding ketone (semicarbazone, m. p. 211°). Addition of acetic anhydride to the mixture failed to improve the yield of dicyclic acetate.

A similar process was applied to the tricyclic diene (XI), 20 g. of which were treated with 170 c.c. of acetic acid and 24 c.c. of phosphoric acid (first dehydrated at 235°). Reaction lasted for 48 hours on the steam-bath and 84 hours at room temperature. The product, isolated as described above, was hydrolysed without purification, and the neutral material fractionated. The fractions boiling between 158° and 182°/0·4 mm. (14·2 g.) all gave the trinitrobenzene addition compound of the uncyclised diene (m. p. 65—66°). The fraction (0·7 g.), b. p. 182—190°/0·4 mm., gave a mixture of trinitrobenzene derivatives, from which after four crystallisations from alcohol the *trinitrobenzene* derivative of 16-methylhexahydrochrysene (XIII) was isolated in yellow needles, m. p. 123° (Found: C, 65·1, 64·85; H, 4·7, 4·5. $C_{19}H_{20},C_6H_3O_6N_3$ requires C, 65·0; H, 5·0%).

This substance was best prepared as follows: 9·0 G. of the diene were heated with an equal weight of phosphoric oxide at 140° for 6 hours. The cooled product was extracted with petrol and distilled. There were obtained 1·4 g., b. p. up to 155°/0·3 mm., and 4·8 g., b. p. 155—175°/ 0·3 mm. The first fraction was a mobile liquid. It yielded a mixture of trinitrobenzene addition compounds, separated by crystallisation from alcohol into the yellow derivative of methylbutylphenanthrene (XII), m. p. 134° (not quite pure), and the orange derivative of the original diene, m. p. 64°. The high fraction was much more viscous. It readily yielded the derivative, m. p. 123°, of the tetracyclic hydrocarbon (XIII). The tetracyclic hydrocarbon was also obtained by cyclisation of the diene with phosphoric oxide at 170°, but not by the use of a mixture of phosphoric oxide and phosphoric acid at 150°.

The trinitrobenzene compound of the tetracyclic hydrocarbon (m. p. 123°) was more stable than that of the diene. It was, however, reconverted into the parent hydrocarbon by treatment with light petroleum and filtration of the solution through an alumina column. The tetracyclic hydrocarbon was a viscous liquid. 710 Mg. of it were heated with 680 mg. of selenium at 310—330° for 19 hours. The residue was extracted with boiling light petroleum (b. p. 40—60°). The extract yielded a crystalline mixture. The mixture was rubbed with a little ether, which left 180 mg. of a grey-green solid, m. p. *ca.* 230°. A solution of this in benzene was run through an alumina column, which removed a trace of selenium. The residue from the benzene was crystallised from benzene–petrol, yielding chrysene, m. p. and mixed m. p. 247—248°; this was further identified as the addition compound with 2 : 7-dinitroanthraquinone.

Attempted Oxidation of 16-*Methylhexahydrochrysene* (XIII).—These negative experiments are briefly summarised below. The general methods were those successful in the dicyclic series (see preceding paper). The hydrocarbon resisted the action of potassium permanganate in acetone, but some oxidation occurred in acetic acid solution : A mixture of 6·4 g. of the tetracyclic hydrocarbon, 20 c.c. of acetic acid, and 40 c.c. of water was treated, first at 0°, then at room temperature, with 200 c.c. of 3% aqueous potassium permanganate. After 24 hours, the mixture was neutralised with aqueous alkali, filtered, and separated into neutral and acid fractions in the usual way. The acid fraction was freed from acetic acid over alkali in a vacuum desiccator. The residue (0·72 g.) partly solidified. It yielded no ketone on pyrolysis with a trace of baryta. The tetracyclic hydrocarbon (1·4 g.) was kept for a week with acetic acid (20 c.c.) and perhydrol (5 c.c.). The product was mainly neutral, but, as it failed to react with lead tetra-acetate, contained no useful amount of diol.

The tetracyclic hydrocarbon was heated with lead tetra-acetate in acetic acid at 70°. The product, isolated in the usual way, was refluxed with methanolic potash and the neutral product was submitted to chromatographic adsorption, a number of fractions being separated arbitrarily. All these yielded the trinitrobenzene compound of the original hydrocarbon, m. p. 123°. The tetracyclic hydrocarbon also failed to react with selenium dioxide in acetic anhydride at 100°.

5·5 G. of the hydrocarbon in 50 c.c. of ethyl acetate were ozonised. The product was boiled with water and further oxidised with alkaline perhydrol. The acidic product, separated by sodium bicarbonate, was a yellow powder, m. p. 165—167° after preliminary softening. It dissolved in aqueous alkali and in organic solvents to give red solutions, and could not be crystallised. Etherification with diazomethane gave a coloured gummy product, which did not lose its colour on chromatographic analysis. It is concluded that this treatment involved a drastic oxidation, ring *C* being probably affected.

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