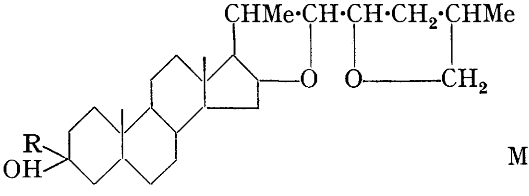
168. *Sapogenins. Part III. The Dehydrogenation Products of Methylsarsasapogenin and Methylcholestanol.*

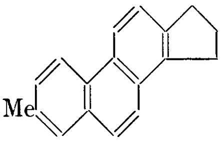
By George A. R. Kon and Aubrey M. Woolman.

The hydrocarbons (II) and (III) have been synthesised and the former has been shown to be identical with one of the dehydrogenation products of methylsarsasapogenin and of methylcholestanol; the compound (III) also has been isolated from the latter source. These results confirm the position previously assigned to the hydroxyl group of sarsasapogenin (Farmer and Kon, J., 1937, 414); they also show that in the dehydrogenation of sterol-like compounds the migration of the angular methyl group from C_{13} to C_{17} is not invariably the rule and that complete elimination of this group can sometimes occur.

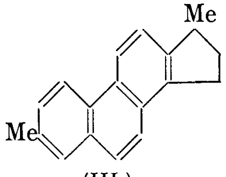
From the work described in Part II (J., 1937, 414) it was concluded that sarsasapogenin is best represented by the structure (I, R = H); the formulation of the side chain is that adopted by Tschesche and Hagedorn (*Ber.*, 1935, **68**, 1412, 2247) for the side chain of tigogenin and this has lately received considerable support from the work of Fieser and Jacobsen (*J. Amer. Chem. Soc.*, 1938, **60**, 28, 2753, 2761). The position of the hydroxyl group on C_3 rests on the results of surface-film measurements (Askew, Farmer, and Kon, J., 1936, 1399) and on the dehydrogenation of methylsarsasapogenin (I, Re = Me) to a mixture of hydrocarbons, also obtained from the analogous methylcholestanol, the principal constituent of which appeared to be the hydrocarbon (II) rather than the expected one (III) :



(I.)



(II.)

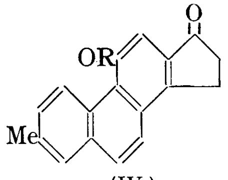


(III.)

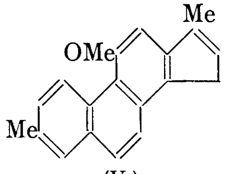
To settle this point, (II) and (III) were synthesised by Robinson's method (J., 1938, 1391) : 2-methyl-6-acetonaphthone (Kon and Weller, preceding paper) was converted into the acetoxy-ketone (IV, R = Ac). This was hydrogenated under drastic conditions, and the crude product (mainly hexahydro) dehydrogenated with palladised charcoal, the hydrocarbon (II) being produced in good yield.

The acetoxy-ketone was then converted into the *methoxy-ketone* (IV, R = Me), which reacted smoothly with methylmagnesium iodide to form the compound (V). Catalytic hydrogenation at room temperature gave the compound (VI), but under drastic conditions a mixture of products was formed which was dehydrogenated to the compound (VI) together with the desired hydrocarbon (III); they were separated without much difficulty.

Proposed alternative syntheses of (II) and (III) were rendered ineffective by unexpected difficulties : (1) the Grignard reagent prepared from 4-bromohydrindene would not react



(IV.)



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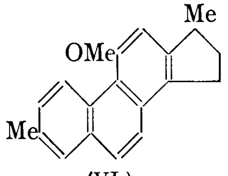
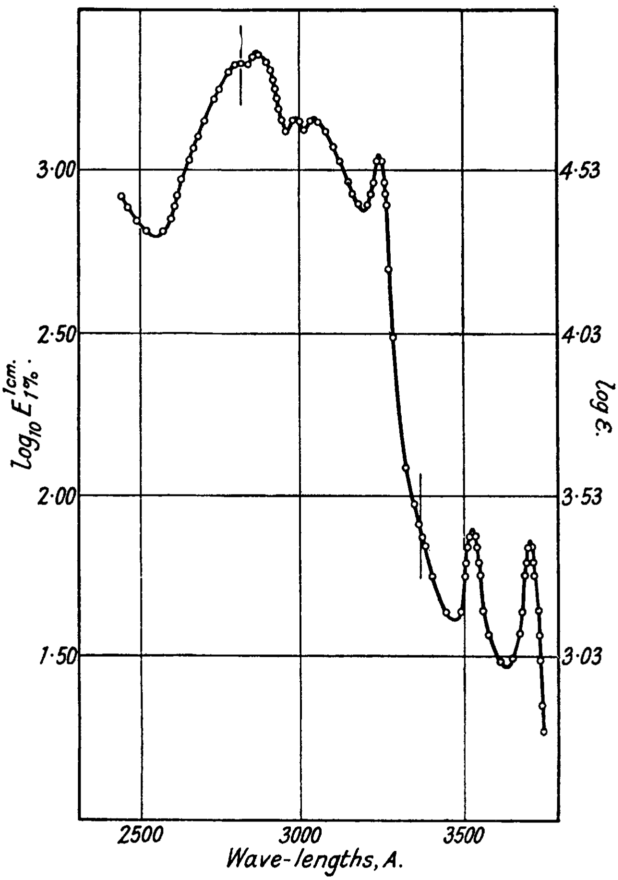


(VI.)

with ethylene oxide to give β-4-hydrindenylethyl alcohol. (2) β-4-*Methoxy*-6-*methyl*-1-*naphthylethyl alcohol*, prepared from the corresponding 1-*bromonaphthalene*, could not be condensed, *via* the bromide, with 2 : 5-dimethyl*cyclo*pentanone. (3) The chloride of 2-*methyl*cyclo*pentenylacetic acid* could not be condensed with the Grignard compound prepared from 1-bromo-4-methoxy-6-methylnaphthalene. A model experiment showed that *cyclo*hexenylacetophenone (Farrow and Kon, J., 1926, 2133) could be smoothly reduced by Clemmensen's method to β-phenylethyl*cyclo*hexene; the analogous cyclo*hexenyl*-1-*acetonaphthone*, prepared from *cyclo*hexenylacetyl chloride and 1-bromonaphthalene, was reduced, and the product cyclised; dehydrogenation then gave chrysene.



The properties of the hydrocarbons (II) and (III) account for the difficulties experienced in dealing with the mixture of hydrocarbons resulting from the dehydrogenation of methylsarsasapogenin and methylcholestanol: the monomethyl compound (II) melts at 132° and forms a sparingly soluble, pale yellow trinitrobenzene complex, m. p. 183°. The dimethyl hydrocarbon (III) is more sparingly soluble in alcohol and higher-melting, but its trinitrobenzene complex is comparatively soluble and melts at 154—155°.

There is little doubt that the pale trinitrobenzene complex previously isolated from the dehydrogenation product of methylcholestanol is identical with the synthetic product from (II) now described. The properties of the other derivatives are also similar and their melting points are not lowered by admixture of the corresponding synthetic derivatives; it is clear, however, that the hydrocarbon isolated in 1936 was not quite pure. Mr. D. P. Riley of Oxford kindly undertook a crystallographic examination of the trinitrobenzene derivatives for us, but his results are not conclusive (p. 798).

The dehydrogenation of 3-methylcholestanol (or 3-*methylcholestene*, which is usually obtained when an excess of Grignard reagent is used in the preparation) has been repeated. A *hydrocarbon*, m. p. 207—208°, was isolated which is evidently a homologue of Diels's hydrocarbon $C_{25}H_{24}$, judged from its composition and absorption spectrum (Figure). From the more soluble components of the mixture was prepared a trinitrobenzene complex, m. p. about 153°, evidently derived from a dimethyl*cyclo*pentenophenanthrene. The hydrocarbon was regenerated from it and repeatedly crystallised, a preparation with the constant m. p. 139—140° being obtained which gave a trinitrobenzene complex, m. p. 154—155°. The hydrocarbon was satisfactorily identified by Mr. Riley as (III).

It can therefore be concluded that both (II) and (III) are formed in this dehydrogenation. This result is of considerable importance and suggests that the elimination of the side chain during the dehydrogenation of compounds of the sterol group is not always accompanied by a migration of the angular methyl group from C_{13} to C_{17}.

The dehydrogenation of methylsarsasapogenin gives a very poor yield of hydrocarbons and we have not yet succeeded in isolating derivatives of (III) in a state of purity; repeated crystallisation of the trinitrobenzene complex, m. p. 174—175°, previously obtained raises the m. p. to 177—179°, but lack of material has prevented the isolation of a complex of constant m. p.; there is little doubt, however, that this compound is identical with the trinitrobenzene derivative of (II).

It is proposed to confirm the results now reported by a further degradation of certain oxidation products of sarsasapogenin; these experiments are now in progress.

EXPERIMENTAL.

o-*Bromobenzylmalonic Acid.*—*o*-Bromobenzyl chloride or bromide was condensed with ethyl sodiomalonate (cf. Fieser and Seligman, *J. Amer. Chem. Soc.*, 1935, **57**, 942); the yield of bromobenzylmalonic ester, b. p. 152°/0·8 mm., was about equal to the weight of the chloride used. The *acid*, obtained by the method used by Fieser and Seligman and crystallised from ethyl acetate–petroleum, had m. p. 149° (decomp.) (Found: Br, 28·9. $C_{10}H_9O_4Br$ requires Br, 29·3%).

β- o-*Bromophenylpropionic Acid.*—The malonic acid was quantitatively decarboxylated by boiling with water for 4 hours; the monobasic acid, which separated as a greasy solid on cooling, was crystallised from benzene–petroleum; m. p. 98° (Gabriel, *Ber.*, 1882, **15**, 2297; Miersch, *ibid.*, 1892, **25**, 2110).

4-*Bromohydrindone.*—37 G. of the above acid were warmed for ½ hour with 37 c.c. of thionyl chloride, and the excess of reagent removed under reduced pressure; dry benzene was then added, and distilled off to ensure the complete removal of thionyl chloride. The residue, dissolved in a little carbon disulphide, was added with constant shaking to an ice-cold suspension of 24 g. of powdered aluminium chloride in 800 c.c. of carbon disulphide; after 20 minutes, a further 8 g. of aluminium chloride were added, and the mixture slowly heated to the b. p. and boiled for 10 minutes. After being kept overnight, the mixture was worked up as usual, and the brownish solid ketone (Miersch, *loc. cit.*) distilled, 27 g. being collected at 125°/1·5 mm.

4-*Bromohydrindene.*—27 G. of the ketone in a little alcohol were boiled for 5 hours with 270 g. of amalgamated zinc, 185 c.c. of hydrochloric acid, and 87 c.c. of water, a further 160 c.c. of acid being added at the end of 3 hours. The hydrocarbon (19·5 g.), isolated by extraction with ether, boiled at 100°/1·5 mm. The compound formed a Grignard reagent with difficulty even under the special conditions recommended by Fieser and Seligman (*loc. cit.*).

1-*Bromo*-4-*methoxy*-6-*methylnaphthalene*.—10 G. of 1-methoxy-7-methylnaphthalene (prepared from 7-methyltetralone : Ruzicka and Mörgeli, *Helv. Chim. Acta*, 1936, **19**, 377) in 80 c.c. of acetic acid were mechanically stirred at 80° while 9 g. of bromine in 20 c.c. of acetic acid were dropped in. The mixture was kept for 10 minutes, then poured into a large volume of water and extracted with ether. The extract was washed with alkali and water, dried, and evaporated, 13 g. of the *bromo*-compound being obtained, b. p. 160—170°/0·8 mm. It solidified and formed needles from petroleum, m. p. 72° (Found : Br, 31·6. $C_{12}H_{11}OBr$ requires Br, 31·8%). On one occasion the bromination proceeded somewhat vigorously and a poor yield of a *dibromo*-compound (1 : 5 ?) was obtained; it boiled at 175°/2 mm. and formed silky needles from petroleum, m. p. 72° (Found : Br, 49·2. $C_{12}H_{10}OBr_2$ requires Br, 48·6%).

β-4-*Methoxy*-6-*methyl*-1-*naphthylethyl Alcohol*.—8·8 G. of the bromo-compound in 34 c.c. of ether were added to 0·9 g. of magnesium, previously activated by heating with a crystal of iodine, and warmed to start the reaction; when no more metal dissolved, the mixture was strongly cooled and vigorously stirred while 1·9 g. of ethylene oxide in 17 c.c of ether were run in. The mixture was allowed to warm to room temperature, boiled for 1 hour, decomposed with ice and hydrochloric acid, and worked up as usual. On distillation 4·6 g. of the *alcohol* were collected at 190—200°/1·5 mm.; this solidified and had m. p. 73° after crystallisation from petroleum. On a larger scale, 53 g. of alcohol were obtained from 140 g. of the bromide (Found : C, 77·6; H, 7·7. $C_{14}H_{16}O_2$ requires C, 77·7; H, 7·5%).

The alcohol gave a moderate yield of the bromide when treated with phosphorus tribromide in benzene solution. The bromide was converted into the Grignard reagent, and this treated with 2-methyl*cyclo*pentanone and also with 2 : 5-dimethyl*cyclo*pentanone. The yield of the fraction presumably representing the required condensation product was negligible in both cases.

Reduction of cyclo*Hexenylacetophenone*.—15 G. of the ketone in 100 c.c. of alcohol were boiled for 18 hours with 158 g. of amalgamated zinc, 200 c.c. of hydrochloric acid, and 50 c.c. of water; the mixture was then cooled and extracted with ether. On distillation 6·3 g. of hydrocarbon were obtained, b. p. 130—135°/4 mm.; on redistillation from sodium this had $d_{4^\circ}^{18\cdot4^\circ}$ 0·95116, n_D 1·53440, $[R_L]_D$ 60·75, in good agreement with the constants of β-phenylethyl*cyclo*hexene (Cook and Hewett, J., 1933, 1098).

$\Delta^{1'}$-cyclo*Hexenyl*-1-*acetonaphthone*.—A Grignard reagent prepared from 90 g. of 1-bromonaphthalene in 180 c.c. of ether was cooled in ice and mixed with 85 c.c. of a saturated solution of anhydrous zinc chloride in ether (prepared by allowing 68 g. of freshly fused zinc chloride to stand with 100 c.c. of dry ether for 24 hours), producing a vigorous reaction; 650 c.c.of toluene were added, and the mixture well shaken. The ether was then distilled off below 30°, and the residue cooled in ice and treated dropwise with 30 g. of *cyclo*hexenylacetyl chloride in toluene with constant shaking. After ¾ hour the mixture was decomposed with ice and dilute sulphuric acid, and the toluene solution washed and dried. After removal of the toluene and some naphthalene 29 g. of a viscous yellow oil distilled at 210—215°/2·5—3 mm.; a semicarbazone could not be obtained (the semicarbazone of *cyclo*hexenylacetophenone also forms with difficulty) (Found : C, 85·9; H, 7·3. $C_{18}H_{18}O$ requires C, 86·4; H, 7·2%).

28 G. of the above *ketone* were reduced as described above and gave 11 g. of hydrocarbon fraction, which was redistilled over sodium; it still contained some oxygen (Found : C, 89·1; H, 8·2%), but was mainly the desired β-1-naphthylethyl*cyclo*hexene (Cook and Hewett, J., 1934, 365).

1 : 2 : 3 : 4 : 11 : 12 : 13 : 14-*Octahydrochrysene*.—6 G. of the above crude hydrocarbon were heated with 12 g. of phosphoric oxide for ¾ hour at 130°. On working up, 1·5 g. of a viscous oil were recovered, which formed a bright yellow *s*-trinitrobenzene *complex*, m. p. 147—148° (Found : C, 64·2; H, 5·5. $C_{18}H_{20},C_6H_3O_6N_3$ requires C, 64·1; H, 5·2%), and on dehydrogenation with selenium gave chrysene, identified by means of the addition product with 2 : 7-dinitroanthraquinone.

2-*Methyl*-$\Delta^{1(?)}$-cyclo*pentenylacetic Acid*.—17 G. of 2-methyl*cyclo*pentanone, 25 g. of methyl bromoacetate, 30 c.c. of benzene, and 5 g. of magnesium were warmed under reflux with a crystal of iodine. The reaction soon started and proceeded with great vigour; it was completed by warming. Ice and dilute sulphuric acid were then added, and the benzene solution washed, dried and distilled, 14 g. of the desired hydroxy-ester being obtained; in another experiment, 62 g. of the ketone gave 55 g. of the hydroxy-ester, b. p. 87°/0·8 mm. This (55 g.) was dehydrated by heating in benzene solution with its own weight of phosphoric oxide for 3 hours. On working up, 31 g. of unsaturated ester, b. p. 75°/1·7 mm., were obtained. The ester was kept for 2 days with a slight excess of cold 5% alcoholic sodium hydroxide, the alcohol removed under reduced pressure, water added, the solution extracted with ether, and the *acid* liberated

(13 g.) and purified by reprecipitation from its solution in aqueous sodium bicarbonate. It solidified but was extremely soluble in organic solvents and was therefore recrystallised from warm water; m. p. 50° (Found: C, 68·5; H, 8·5. $C_8H_{12}O_2$ requires C, 68·5; H, 8·6%).

Furfurylidene-2-methyl-6-acetonaphthone.—An ice-cold solution of 1 g. of sodium in 40 c.c. of alcohol was added to 19 g. of 2-methyl-6-acetonaphthone and 13 c.c. of furfural in 20 c.c. of alcohol. The mixture became hot and crystallisation rapidly set in. After some hours the solid was collected and recrystallised from alcohol, 23 g. of the pure *ketone* being obtained in pale yellow needles, m. p. 121° (Found: C, 82·6; H, 5·4. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3%). The compound (40·5 g.) is equally readily prepared from the mixture (55 g.) of 2-methyl-6- and -8-acetonaphthones formed from acetyl chloride and 2-methylnaphthalene (Kon and Weller, *loc. cit.*). The furfurylidene compound of the 2 : 8-ketone is evidently much more soluble and remains in the mother-liquor.

$\delta\eta$-Diketo-η-(6-methyl-2-naphthyl)heptoic Acid.—The hydrolysis of the furfurylidene ketone (40·5 g.) was carried out exactly as described by Robinson (*loc. cit.*, p. 1394), successive crops of the *acid* being obtained (23 g.). The acid crystallised from ethyl acetate (charcoal) in leaflets, m. p. 181° (Found: C, 72·3, 72·2; H, 6·2, 6·0. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·1%); it formed a bright red 2 : 4-dinitrophenylhydrazone, m. p. 145—146°.

3-(*6'-Methyl-2'-naphthyl*)-Δ^2-cyclo*penten-1-one-2-acetic Acid.*—15 G. of the powdered diketo-acid were kept for 1 hour with 30 g. of potassium hydroxide in 1·5 l. of water at 95—100°; the solution was then acidified. The *acid* crystallised from ethyl acetate (charcoal) in short stout needles, m. p. 188° (Found: C, 77·1; H, 5·7. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·8%).

3'-Keto-4-acetoxy-7-methyl-1 : 2-cyclo*pentenophenanthrene* (IV, R = Ac).—5 G. of the above acid were boiled for ½ hour with 37·5 c.c. of acetic anhydride. On cooling and addition of methyl alcohol the new *compound* crystallised; a little more was obtained from the concentrated mother-liquor (yield, 5 g.); it separated from ethyl acetate in needles, m. p. 224° (decomp.) (Found: C, 79·3; H, 5·7. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%). An attempt to reduce the compound by Clemmensen's method resulted in hydrolysis to the *hydroxy-ketone*, which formed a sparingly soluble, sandy powder, m. p. 290° (decomp.) (Found: C, 82·2; H, 5·7. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·4%).

7-Methyl-1 : 2-cyclo*pentenophenanthrene* (II).—2·2 G. of the pure acetoxy-ketone in 200 c.c.* of acetic acid (distilled over chromium trioxide) were shaken with 0·3 g. of Adams's catalyst in an atmosphere of hydrogen at 80—85° for 2½ days; about 12 atoms of hydrogen were absorbed. After removal of the catalyst most of the solvent was distilled, and the product isolated by addition of water and extraction with ether, 2 g. of an almost colourless, viscous oil being obtained. This was heated with an equal weight of 10% palladised charcoal for 1½ hours at 320°. The *hydrocarbon* was extracted with petroleum, and the solution percolated through a column of activated alumina and evaporated, 0·5 g. of a colourless solid being obtained. It crystallised from alcohol in iridescent plates, m. p. 132° (Found: C, 93·0; H, 7·0. $C_{18}H_{16}$ requires C, 93·1; H, 6·9%). The picrate formed orange needles from alcohol, m. p. 143—144°, the *styphnate* long golden needles, m. p. 182—183° (Found: C, 60·4; H, 4·2. $C_{18}H_{16},C_6H_3O_8N_3$ requires C, 60·4; H, 4·1%), and the *s*-trinitrobenzene *compound* yellow needles, m. p. 183—183·5° (Found: C, 64·9; H, 4·3; $C_{18}H_{16},C_6H_3O_6N_3$ requires C, 64·7; H, 4·3%).

Mr. D. P. Riley has made a comparison of the trinitrobenzene derivatives of the dehydrogenation product of methylcholestanol, m. p. 181—182° (A), that of the synthetic hydrocarbon, m. p. 183—183·5° (B), and the specimen derived from methylsarsasapogenin m. p. 177—179° (C), and reports as follows: "Each specimen was recrystallised from alcohol. The crystals were in each case yellow monoclinic blades elongated along [100] or [001], with [010] markedly developed. The angle α between the length of the blade and the fast optical extinction direction varied. Approximate mean values for α were for (A), 10·5°, (B), 12°, (C), 7°. *X*-Ray oscillation photographs were taken of each crystal rotating about the length of the blade. The photographs were not good, but showed that the unit-cell spacings were very nearly identical. In view of the differences in optical properties and of the poor quality of the photographs it is impossible unequivocally to state that (A), (B), and (C) are identical. The differences in optics may be caused by varying amounts of trinitrobenzene in the crystals; on the other hand, the addition of trinitrobenzene may mask slight differences in them. For these reasons it would be desirable to examine the original hydrocarbons." It is hoped to institute such a comparison when sufficient pure material is available.

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* We are greatly indebted to Sir R. Robinson and Dr. H. N. Rydon for supplying the details of the procedure which they have used for the conversion of acetoxyketo*cyclo*pentenophenanthrene into *cyclo*pentenophenanthrene

3′-*Keto*-4-*methoxy*-7-*methyl*-1 : 2-cyclo*pentenophenanthrene* (IV, R = Me).—7 G. of the powdered acetoxy-ketone were boiled for $\frac{1}{2}$ hour with 35 c.c. of alcohol and 70 c.c. of 40% aqueous sodium hydroxide. Methyl sulphate was then added a little at a time until the yellow colour of the solution was discharged and did not reappear on addition of more alkali. The solution was cooled, and the solid (6·5 g.) collected; the filtrate gave no appreciable precipitate on acidification. The *methoxy*-compound, crystallised from ethyl acetate–alcohol (charcoal), then from benzene–petroleum, formed long needles, m. p. 190—191° (Found : C, 82·6; H, 5·7. $C_{19}H_{16}O_2$ requires C, 82·5; H, 5·8%). The ketone was recovered unchanged after an attempted reduction by Clemmensen's method with addition of anisole (Robinson).

4-*Methoxy*-3′ : 7-*dimethyl*-1 : 2-cyclo*pentadienophenanthrene* (V).—A suspension of 2 g. of the finely powdered methoxy-ketone in 20 c.c. of ether was slowly added to an ice-cold Grignard solution made from 0·34 g. of magnesium and 2 g. of methyl iodide; the mixture was then boiled for 2—3 hours. After the usual working up, a pale yellow solid was obtained; it crystallised from alcohol or aqueous acetone (charcoal) in very small needles, m. p. 130—131°; on a larger scale 6 g. were obtained from 7 g. of the ketone (Found : C, 87·9; H, 6·9. $C_{20}H_{18}O$ requires C, 87·5; H, 6·6%).

4-*Methoxy*-3′ : 7-*dimethyl*-1 : 2-cyclo*pentenophenanthrene* (VI).—1 G. of the above compound, dissolved in alcohol, was shaken with 0·05 g. of Adams's catalyst in hydrogen, the theoretical amount for the saturation of one double bond being absorbed in 16 hours. After removal of the catalyst the solution was evaporated, and the residue taken up in petroleum (b. p. 60—80°) and percolated through a column of activated alumina. A colourless solid was recovered and crystallised from methyl alcohol; m. p. 83—84° (Found : C, 86·9, 87·0; H, 7·1, 7·1. $C_{20}H_{20}O$ requires C, 86·9; H, 7·3%); it was very soluble in organic solvents. The *s*-trinitrobenzene *compound* formed felted orange needles, m. p. 184—185°, very sparingly soluble in alcohol, and separated almost completely from the solution on cooling, leaving a colourless filtrate (Found : C, 64·0; H, 4·5. $C_{20}H_{20}O,C_6H_3O_6N_3$ requires C, 63·8; H, 4·7%).

3′ : 7-*Dimethyl*-1 : 2-cyclo*pentenophenanthrene* (III).—4·5 G. of the compound (V) were hydrogenated at 80—85° as described on p. 798; hydrogen corresponding to about five double bonds was absorbed in $2\frac{1}{2}$ days. The crude oil recovered was heated with palladised charcoal, 2·2 g. of a colourless non-homogeneous solid being recovered after treatment with alumina. It was converted into the *s*-trinitrobenzene complex, which was extracted three times with boiling alcohol. The portion which was not dissolved melted at 183—184° after two crystallisations and was evidently derived from the compound (VI). The alcoholic extracts were cooled, filtered, and evaporated to dryness, and the solid extracted with petroleum (b. p. 60—80°) until the extract was colourless; the combined extracts were then percolated through a column of activated alumina, which decomposed the complex and retained any trinitrobenzene dissolved by the petroleum. On evaporation a colourless solid, m. p. 135°, was recovered; it crystallised from alcohol in plates, m. p. 139—140° (Found : C, 92·6; H, 7·5. $C_{19}H_{18}$ requires C, 92·6; H, 7·4%). The orange-yellow *picrate* had m. p. 128° (Found : C, 63·6; H, 4·5. $C_{19}H_{18},C_6H_3O_7N_3$ requires C, 63·1; H, 4·5%), the *styphnate* formed yellow needles, m. p. 161° (Found : C, 61·0; H, 4·3. $C_{19}H_{18},C_6H_3O_8N_3$ requires C, 61·1; H, 4·3%), the *s*-trinitrobenzene *compound* formed deep yellow needles, m. p. 154—155° (Found : C, 65·6; H, 4·7. $C_{19}H_{18},C_6H_3O_6N_3$ requires C, 65·3; H, 4·6%).

3-*Methylsarsasapogenin*.—This compound was prepared as before. Repeated crystallisation of the carbinol raised the m. p. to 188—189°, $[\alpha]_D - 88°$ ($c = 1·2478$ in chloroform). The compound frequently melts much lower and can be purified by means of digitonin, the portion not combined showing the above m. p.; the isomeride forming a digitonide has not yet been obtained pure.

3-*Methylcholestene*.—This compound is generally obtained if an excess of methylmagnesium iodide is used in the preparation of methylcholestanol; it has $[\alpha]_D + 16°$ ($c = 1·602$ in chloroform).

Dehydrogenation of 3-*Methylcholestene*.—An attempt was made to use acetanilide as a solvent as recommended by Diels and Stĕphan (*Annalen*, 1937, **527**, 279), but scarcely any dehydrogenation took place. 88 G. of methylcholestene were dehydrogenated by the method previously described; the product, fractionally distilled at 1·5 mm., gave a few drops below 170°, then (1) 170—200°, 10 g., mobile oil; (2) 200—220°, 8 g. which solidified; (3) 220—230°, 14 g., which solidified; (4) 230—255°, 13 g., viscous oil. These fractions were each separately treated with *s*-trinitrobenzene; fraction (1) in particular gave a complex, m. p. about 150° after three crystallisations from alcohol, apparently derived from a dimethyl*cyclo*pentenophenanthrene (Found : C, 65·9, 65·6; H, 4·6, 4·4%). The crude trinitrobenzene derivatives were decomposed as described on p. 799 and 5 g. of an almost colourless, solid hydrocarbon were recovered; after several crystallisations a hydrocarbon, m. p. 129—132°, was obtained and reconverted into the trinitrobenzene complex, m. p. 150° after crystallisation. From 2·8 g. of this material, 1·8 g. of hydrocarbon were regenerated and recrystallised from alcohol. After six crystallisations the m. p. remained constant at 139—140°, unchanged by the compound (III) (Found: C, 92·3; H, 7·8. $C_{19}H_{18}$ requires C, 92·6; H, 7·4%). The *s*-trinitrobenzene compound formed from the pure hydrocarbon had m. p. and mixed m. p. 154—155° after one crystallisation from alcohol (Found: C, 65·4, 65·2; H, 4·7, 4·3. Calc. for $C_{19}H_{18},C_6H_3O_6N_3$: C, 65·3; H, 4·6%). The styphnate had m. p. and mixed m. p. 161°.

Mr. D. P. Riley has compared the above hydrocarbon with the synthetic specimen of (III) and reports as follows: " In both cases uniformly extincting sheets grown from the melts were examined. The sheets were orthorhombic with optics $a = \alpha$, $b = \beta$, $c = \gamma$ in both cases. The birefringence was medium (positive). *X*-Ray oscillation photographs were taken with the crystal rotating about the slow extinction direction [010], and about the perpendicular to the plane of the sheet, *i.e.*, [001], in both cases. The unit-cell spacings and relative intensities of reflection were the same for both specimens and these are therefore identical."

The hydrocarbon mixture boiling above 240°/1·5 mm. deposited from its solution in benzene a solid, which was repeatedly crystallised from this solvent and formed fine needles, m. p. 207—208° (Found: C, 92·5; H, 7·5. $C_{26}H_{26}$ requires C, 92·3; H, 7·7%). The *hydrocarbon* did not react with *s*-trinitrobenzene, but formed a brilliant scarlet *derivative* with 2 : 7-dinitroanthraquinone, m. p. 235° (Found: C, 75·3, 75·2; H, 5·0, 4·9. $C_{40}H_{32}O_6N_2$ requires C, 75·4; H, 5·1%).

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