106. *Synthesis of Alkylphenanthrenes. Part VI. Attempts to synthesise the Hydrocarbon "$C_{16}H_{14}$," derived from Strophanthidin.*

By Robert Downs Haworth, Cecil Robert Mavin, and George Sheldrick.

A comparison of the absorption spectra and the *X*-ray crystallographic measurements of "$C_{18}H_{16}$," obtained from the sterols and the bile acids, "$C_{16}H_{14}$," obtained from strophanthidin, and various alkylphenanthrenes has demonstrated that the first two hydrocarbons are probably phenanthrene derivatives (Rosenheim and King, *J. Soc. Chem. Ind.*, 1932, 954; 1933, 10, 299; Bernal, *ibid.*, 1933, 10; Bernal and Crowfoot, *ibid.*, 1933, 729). At the commencement of the present work, there was a possibility that "$C_{18}H_{16}$" was a phenanthrene derivative in which quinone formation was inhibited by alkyl substituents in the 9- or 10-position, but this view has now been abandoned and "$C_{18}H_{16}$" is considered to be a methyl*cyclo*pentenophenanthrene. The hydrocarbon "$C_{16}H_{14}$," obtained by Jacobs and Fleck (*Science*, 1931, 133; *J. Biol. Chem.*, 1932, **97**, 57) by selenium dehydrogenation of strophanthidin, yielded an *o*-quinone, $C_{16}H_{12}O_2$, and these authors suggested that it was a dimethylphenanthrene, a suggestion which is supported by the physical evidence mentioned above.

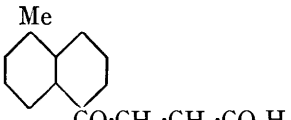
The object of the present research was to determine the structure of these two hydrocarbons synthetically. After synthesising 2 : 9-dimethylphenanthrene, other developments in connexion with "$C_{18}H_{16}$" caused us to abandon experiments in this direction, and to concentrate our attention on the strophanthidin hydrocarbon, "$C_{16}H_{14}$," m. p. 125—126°. This hydrocarbon, which must be unsubstituted in the 9- and 10-positions, in order to account for the formation of the *o*-quinone, differs from the known 1 : 4-, 1 : 7-, and 1 : 9-dimethylphenanthrenes. The present communication describes the synthesis of the remaining 9 : 10-unsubstituted dimethylphenanthrenes, with the exception of 3 : 5- and 4 : 5-dimethylphenanthrene, but none of the synthetical hydrocarbons is identical with "$C_{16}H_{14}$."

Further, "$C_{16}H_{14}$" differs from 1-, 2-, and 3-ethylphenanthrenes. 1-Ethylphenanthrene has been described by Pschorr (*Ber.*, 1906, **39**, 3127) and Gadamer (*Arch. Pharm.*, 1911, **249**, 667), who obtained it by the distillation of methoxy-1-vinylphenanthrenes of alkaloidal origin with zinc dust. The constants now recorded for 1-*ethylphenanthrene* differ considerably from those previously reported, and as the synthetical hydrocarbon yields phenanthrene-1-carboxylic acid on oxidation, it is concluded that the hydrocarbon obtained previously is probably a polymeride of 1-vinylphenanthrene.

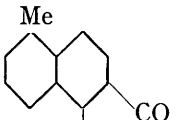
Although the analytical figures recorded for the hydrocarbon by Jacobs and Fleck are in excellent agreement with the formula $C_{16}H_{14}$, its possible identity with a homologue has been tested by the synthesis of 1-*propyl*-, 1- and 2-iso*propyl*-, 1-*methyl*-2-*ethyl*-, and 2-*methyl*-1-*ethyl*-*phenanthrene*, all of which, however, differ from "$C_{16}H_{14}$." The selection of these hydrocarbons was determined by three considerations: (1) the similarity in cell dimensions of retene and "$C_{16}H_{14}$" encouraged us to prepare the *iso*propyl derivatives; (2) the possibility of a close relationship between strophanthidin and the sterols suggested that one or more of the above hydrocarbons might be produced from a *cyclo*pentenophenanthrene during selenium dehydrogenation; (3) an examination of the synthetical dimethylphenanthrenes showed that symmetrical and 1 : 2-disubstituted phenanthrenes, as a rule, have relatively high melting points, thus indicating that "$C_{16}H_{14}$" may be either a 1 : 2- or a symmetrically disubstituted phenanthrene.

The syntheses employed were either the general methods used in earlier parts of this

series, or the method of Bardhan and Sengupta (J., 1932, 2520, 2798). One point, which explains our failure to prepare 3 : 5- and 4 : 5-dimethylphenanthrene, requires special mention. The synthesis of 1 : 8-*dimethylphenanthrene* commenced with 5-cyano-1-methylnaphthalene, which was converted *via* 5-methyl-1-naphthyl methyl ketone, β-(5-*methyl*-1-*naphthoyl*)*propionic acid* (I), and 1-*keto*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II) into 1 : 8-dimethylphenanthrene, m. p. 191°.



(I.)



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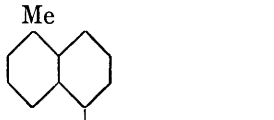

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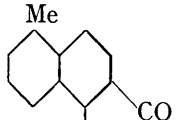
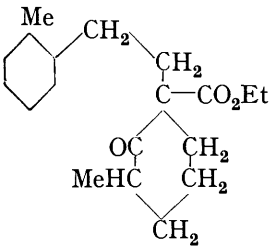
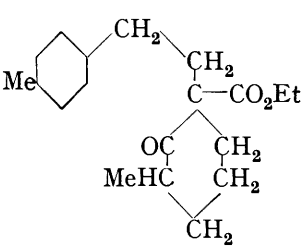


(IV.)

An attempted synthesis of 1 : 5-dimethylphenanthrene gave remarkable results. The methyl ester of (I) reacted with methylmagnesium iodide to give a poor yield of (III), which was converted into 1-*keto*-4 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IV). This was reduced by Clemmensen's method, and the product dehydrogenated in the usual way. The principal product was identical with 1 : 8-dimethylphenanthrene, obtained as described above, and after prolonged fractional crystallisation, small amounts of an isomeric hydrocarbon, m. p. 51—52°, considered to be 1 : 5-*dimethylphenanthrene*, were isolated. In an attempt to synthesise 1 : 5-dimethylphenanthrene by another method, β-*o*-tolylethyl bromide and ethyl potassio-6-methyl*cyclo*hexanone-2-carboxylate were combined to give *ethyl* 2-(β-o-*tolylethyl*)-6-*methyl*cyclo*hexanone*-2-*carboxylate* (V). This was reduced, and the product cyclised and dehydrogenated, as described by Bardhan and Sengupta (*loc. cit.*) for analogous cases, but as 1 : 8-dimethylphenanthrene and smaller amounts of 1 : 5-dimethylphenanthrene, m. p. 51—52°, were again isolated, it was concluded that the abnormal result was due to migration of a methyl group from position 4 to position 1. A similar abnormal result was obtained during an attempted synthesis of 3 : 5-dimethyl-



(V.)

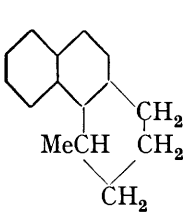


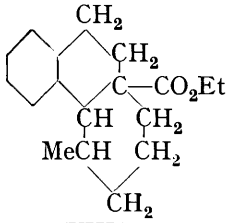
(VI.)

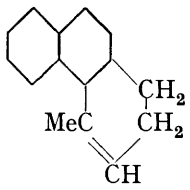
phenanthrene. *Ethyl* 2-(β-p-*tolylethyl*)-6-*methyl*cyclo*hexanone*-2-*carboxylate* (VI), prepared from β-*p*-tolylethyl bromide and ethyl potassio-6-methyl*cyclo*hexanone-2-carboxylate, was reduced, and the product cyclised and dehydrogenated. A hydrocarbon identical with 1 : 6-*dimethylphenanthrene* was isolated and, although other substances were produced during the dehydrogenation, it has not been possible to isolate the expected 3 : 5-dimethylphenanthrene.

In other cases of similar type, the dehydrogenated mixture has proved incapable of resolution into pure compounds. For instance, the dehydrogenation of 4-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (VII), obtained from 4-methyl-1 : 2-dihydrophenanthrene (IX) by catalytic reduction, is abnormal; a hydrocarbon mixture, $C_{15}H_{12}$, is obtained, from which neither 1- nor 4-methylphenanthrene has so far been isolated. The dehydrogenation of 4-methyl-1 : 2-dihydrophenanthrene proceeds normally (J., 1932, 1128) to yield 4-methylphenanthrene. This result has been confirmed, and the evidence so far obtained suggests that migration of alkyl groups from position 4 to 1 occurs when compounds of type (VII) and (VIII) (but not IX) are dehydrogenated with selenium. Before these abnormalities had been realised, an attempt to synthesise 2 : 4-dimethylphenanthrene, from β-(1-

naphthoyl)*iso*butyric acid, along lines similar to those described above in the attempted synthesis of 1 : 5-dimethylphenanthrene, gave an oil, $C_{16}H_{14}$, which was considered to be

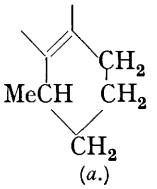

(VII.)

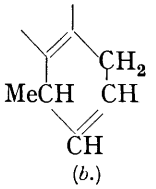

(VIII.)

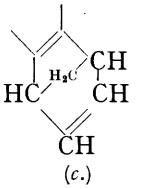

(IX.)

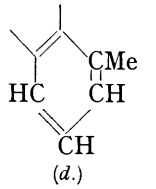
the desired hydrocarbon. The picrate, m. p. 118°, quinone, m. p. 156°, and quinoxaline, m. p. 186°, gave the correct analytical results and simulated homogeneous compounds. However, 2 : 4-*dimethylphenanthrene*, prepared by a method in which migration was excluded, proved to be a solid, m. p. 111°, giving a *picrate*, *quinone*, and *quinoxaline* melting at 139°, 169°, and 156° respectively. It is concluded that the earlier synthesis led to an inseparable mixture of isomeric hydrocarbons.

Elimination of methyl groups during the conversion of hydroaromatic into aromatic compounds is well known, but this is the first observation of the migration of a methyl group during selenium dehydrogenation. The diagnostic value of this method of determining structure is therefore open to criticism, or at any rate requires extreme caution in the interpretation of results. As far as we are aware, there is no analogy to this migration in the literature. The presence of a hydrogen atom in the 4-position is essential for the occurrence of migration, suggesting that this hydrogen atom resists dehydrogenation on account of steric factors. The normal route to the aromatic condition, involving the elimination of this hydrogen atom, is therefore inhibited, and it is tentatively suggested that the migration of the methyl group and the aromatic condition are attained by a mechanism indicated by the partial formulæ (*a*) to (*d*).


(*a*.)


(*b*.)


(*c*.)


(*d*.)

The migration of alkyl groups and other routes to 1 : 5-, 3 : 5-, and 4 : 5-dimethylphenanthrenes are being examined further.

(Addendum, April 12th, 1934.)

Recently Elderfield and Jacobs (*Science*, 1934, **79**, 279) have established a connexion between strophanthidin and the sterols; 150 g. of strophanthidin, dehydrogenated under carefully regulated temperature conditions, yielded 0·5 g. of "$C_{18}H_{16}$," obtained from the sterols. They suggest that "$C_{16}H_{14}$," described previously, is a mixture of "$C_{18}H_{16}$" and a dimethylphenanthrene, the latter being responsible for the *o*-quinone, obtained by oxidising the mixture with chromic acid.

However, the quinone, m. p. 208—210°, and quinoxaline, m. p. 187—188°, do not correspond with the derivatives of any known dimethylphenanthrene. 1 : 2 : 7-Trimethylphenanthrene (J., 1932, 2250) gives a quinone, m. p. 209—210°, and a quinoxaline, m. p. 184—185°, but a depression in melting point of about 20° was observed when the synthetic quinoxaline was mixed with a specimen of quinoxaline kindly supplied by Professor W. A. Jacobs.

Experimental.

The general methods employed follow closely those described in earlier parts of this series. Clemmensen reduction processes and cyclisations to ketotetrahydrophenanthrenes are described

in Part I (J., 1932, 1128), the condensation of Grignard reagents with derivatives of naphthoylpropionic acid and the reduction of pentenoic acids with phosphorus and hydriodic acid in Part II (*ibid.*, p. 1789), and the conversion of naphthyl alkyl ketones into naphthoylpropionic acids in Part III (*ibid.*, p. 2249). The dihydrophenanthrene derivatives now described were obtained by dehydrating the carbinols, prepared by the action of Grignard reagents on ketotetrahydrophenanthrenes, with 98% formic acid (2 vols.) at 100° for ½ hour. The method of Bardhan and Sengupta (*loc. cit.*) has been used in several cases without important modification.

1 : 2-*Dimethylphenanthrene*.—1 : 2-*Dimethyl*-3 : 4-*dihydrophenanthrene*, obtained in 90% yield from 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (J., 1932, 1132) and methylmagnesium iodide, crystallised from methyl alcohol in colourless leaves, m. p. 99—100° (Found : C, 91·9; H, 7·7. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%). The *picrate* separated from methyl alcohol in slender, maroon prisms, m. p. 121—122° (Found : C, 60·3; H, 4·4. $C_{22}H_{19}O_7N_3$ requires C, 60·4; H, 4·4%). 1 : 2-Dimethylphenanthrene, obtained in 70% yield by the action of selenium on the dihydro-derivative, crystallised from acetic acid or alcohol in colourless leaflets, m. p. 142—143° (Found : C, 92·9; H, 7·0. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). The picrate, orange needles, m. p. 153—154°, from alcohol (Found : C, 60·7; H, 3·7. Calc. for $C_{22}H_{17}O_7N_3$: C, 60·7; H, 3·9%), *styphnate*, slender yellow needles, m. p. 153°, from alcohol (Found : C, 58·6; H, 3·8. $C_{22}H_{17}O_8N_3$ requires C, 58·5; H, 3·7%), *quinone*, slender orange prisms, m. p. 213—214°, from acetic acid (Found : C, 81·4; H, 5·0. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%), and *quinoxaline*, slender cream prisms, m. p. 143—144°, from alcohol or acetic acid (Found : N, 8·8. $C_{22}H_{16}N_2$ requires N, 9·1%), were prepared. After the completion of this synthesis, Butenandt, Weidlich, and Thompson recorded a similar synthesis and reported 140° and 148° as the m. p.'s of the hydrocarbon and its picrate respectively (*J. Soc. Chem. Ind.*, 1933, 331; *Ber.*, 1933, **66**, 601).

1 : 3-*Dimethylphenanthrene*.—*Methyl* β-(2-*naphthoyl*)iso*butyrate*, colourless pearly plates, m. p. 74—75°, from methyl alcohol (Found : C, 74·9; H, 6·2. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·2%), obtained in 95% yield by the action of methyl-alcoholic hydrogen chloride on the corresponding acid (J., 1932, 1131), reacted with methylmagnesium iodide, giving a 75% yield of γ-2-*naphthyl*-α-*methyl*-Δ^{β}-*pentenoic acid*, which crystallised from methyl alcohol in colourless prisms, m. p. 168—169° (Found : equiv., 239. $C_{16}H_{16}O_2$ requires equiv., 240). This acid was reduced and cyclised to give a 60% yield (calc. on the pentenoic acid used) of 4-*keto*-1 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b. p. 167—169°/0·3 mm. (Found : C, 85·5; H, 7·0. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%). The latter was converted in 60% yield into 1 : 3-dimethylphenanthrene, which crystallised from alcohol in colourless needles, m. p. 75—76° (Found : C, 92·8; H, 6·7%). The picrate, slender orange needles, m. p. 154—155°, from alcohol (Found : N, 9·8. Calc. for $C_{22}H_{27}O_7N_3$: N, 9·7%), *styphnate*, orange prisms, m. p. 165—166°, from alcohol (Found : C, 58·2; H, 3·8%), quinone, orange prisms, m. p. 215—216°, from alcohol (Found : C, 81·0; H, 4·6%), and *quinoxaline*, slender yellow prisms, m. p. 154—155°, from acetic acid (Found : C, 85·4; H, 5·2. $C_{22}H_{16}N_2$ requires C, 85·7; H, 5·2%), were prepared. Bogert and Stamatoff (*Rec. trav. chim.*, 1933, 584) have prepared this hydrocarbon by another method and give 76—77°, 153—155°, and 218—219° (corr.) as the m. p.'s of the hydrocarbon, its picrate, and quinone respectively.

1 : 6-*Dimethylphenanthrene*.—(a) Ethyl 5-methyl*cyclo*hexanone-2-carboxylate (Kotz and Hesse, *Annalen*, 1905, **342**, 321; 80% yields were obtained by allowing ethyl oxalate and 3-methyl*cyclo*hexanone to remain for 12 hours in the ice chest) was converted into its potassio-derivative and condensed with *o*-tolylethyl bromide (Bardhan and Sengupta, *loc. cit.*). *Ethyl* 2-(β-o-*tolylethyl*)-5-*methyl*cyclo*hexanone*-2-*carboxylate*, b. p. 170—175°/0·4 mm. (Found : C, 75·5; H, 8·8. $C_{19}H_{26}O_3$ requires C, 75·5; H, 8·6%), obtained in 50% yield, was converted in 15% yield into 1 : 6-dimethylphenanthrene by the method of Bardhan and Sengupta. (b) β-*p*-Tolylethyl alcohol (Shoesmith and Connor, J., 1927, 1770), obtained in 55% yield by the action of ethylene oxide on *p*-tolylmagnesium bromide, was converted into β-*p*-tolylethyl bromide in 90% yield by heating at 100° for 12 hours with 30% hydrogen bromide in acetic acid (7 vols.). This bromide and ethyl 6-methyl*cyclo*hexanone-2-carboxylate (Kotz and Michels, *Annalen*, 1906, **348**, 94) gave a 50% yield of *ethyl* 2-(β-p-*tolylethyl*)-6-*methyl*cyclo*hexanone*-2-*carboxylate*, b. p. 170—175°/0·4 mm. (Found : C, 75·3; H, 8·7%), which was converted in 10% yield into 1 : 6-dimethylphenanthrene. The mother-liquors yielded uncrystallisable oils. 1 : 6-*Dimethylphenanthrene* crystallised from methyl alcohol in colourless plates, m. p. 87—88° (Found : C, 93·6; H, 6·8%). The *picrate*, yellow needles, m. p. 134°, from alcohol (Found : C, 60·9; H, 4·2%), *quinone*, orange plates, m. p. 200°, from alcohol (Found : C, 81·2; H, 5·0%), and

quinoxaline, slender cream needles, m. p. 189°, from acetic acid–chloroform (Found: C, 85·5; H, 5·3%), were prepared.

1 : 8-*Dimethylphenanthrene*.—5-Methyl-1-naphthyl bromomethyl ketone (J., 1932, 2722) and ethyl sodiomalonate reacted to give, ultimately, a 55% yield of β-(5-*methyl*-1-*naphthoyl*)-*propionic acid* (I), which crystallised from benzene or methyl alcohol in stout colourless prisms, m. p. 169—170° (Found: equiv., 242. $C_{15}H_{14}O_3$ requires equiv., 242). The methyl ester, b. p. 195—197°/0·3 mm., solidified on long standing. The keto-acid, dissolved in acetic acid (6 vols.), was reduced in 90% yield to γ-(5-*methyl*-1-*naphthyl*)*butyric acid*, which crystallised from a small amount of methyl alcohol in rosettes of silky needles, m. p. 128—129° (Found: equiv., 227. $C_{15}H_{16}O_2$ requires equiv., 228). 1-*Keto*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II), obtained in 70% yield, crystallised from benzene–light petroleum (b. p. 60—80°) in colourless plates, m. p. 164—165° (Found: C, 85·4; H, 6·7. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%), sparingly soluble in ether. This cyclic ketone was converted in 95% yield into crystalline 1 : 8-dimethyl-3 : 4-dihydrophenanthrene, which was not characterised further, but was converted in 75% yield into 1 : 8-*dimethylphenanthrene*. This hydrocarbon, which is sparingly soluble in boiling alcohol or cold acetic acid and readily soluble in chloroform, crystallised from acetic acid or benzene in glistening plates, m. p. 191—192° (Found: C, 93·1; H, 7·2%). The *picrate*, yellow needles, m. p. 151—152°, from alcohol containing a little picric acid (Found: N, 9·4. $C_{22}H_{17}O_7N_3$ requires N, 9·7%), dissociates on crystallisation from alcohol. The *quinone*, deep orange plates, m. p. 190°, from acetic acid (Found: C, 80·8; H, 4·9%), and *quinoxaline*, cream needles, m. p. 178°, from acetic acid (Found: N, 9·0%), were prepared.

1 : 5-*Dimethylphenanthrene*.—(a) The pentenoic acid (III), obtained as an oil from methylmagnesium iodide and methyl β-(5-methyl-1-naphthoyl)propionate (see above), was reduced with phosphorus and hydriodic acid, and the product cyclised. 1-*Keto*-4 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IV), obtained in 20% yield (calc. on the ester used), crystallised from light petroleum (b. p. 40—60°) or methyl alcohol in colourless nodules, m. p. 104—106° (Found: C, 85·4; H, 6·9. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%). This was reduced and dehydrogenated.

(b) β-*o*-Tolylethyl bromide and ethyl potassio-6-methyl*cyclo*hexanone-2-carboxylate gave a 60% yield of *ethyl* 2-(β-o-*tolylethyl*)-6-*methyl*cyclo*hexanone*-2-*carboxylate*, b. p. 170—172°/0·4 mm. (Found: C, 75·4; H, 8·6%), which was reduced, cyclised, and dehydrogenated.

The dehydrogenation products from experiments (a) and (b) gave similar results when examined in the following manner. The hydrocarbon mixture, isolated with chloroform, was distilled in a vacuum over sodium, and the fraction, b. p. 190—220°/12 mm., collected, dissolved in much alcohol, and fractionally crystallised. The first five fractions, m. p. 186—190°, 180—185°, 175—177°, 170—172°, and 165—167°, were combined and crystallised from benzene, giving 1 : 8-dimethylphenanthrene, m. p. 191° (yield, *ca.* 10%, calc. on the hydrogenated phenanthrene used), identical with that described above. The combined benzene and alcohol mother-liquors were evaporated and the residue was converted into picrate in alcoholic solution. After two crystallisations from alcohol, a picrate was obtained in bronze prisms, m. p. 127—129°, unchanged by further crystallisation (Found: C, 60·6; H, 3·7%), but decomposition with ammonia yielded a hydrocarbon mixture, which was subjected to a systematic fractional crystallisation from alcohol. The head fractions gave 1 : 8-dimethylphenanthrene (1% yield), the tail fractions were oils, and from the middle fractions, 1 : 5-*dimethylphenanthrene* was isolated in 2—3% yield. This hydrocarbon crystallised from methyl alcohol in small colourless plates, m. p. 57—58° (Found: C, 93·1; H, 7·0%). The *picrate*, orange needles, m. p. 134—135°, from methyl alcohol (Found: C, 60·7; H, 3·7%), was reconverted into the hydrocarbon, which again melted at 57—58°.

2 : 3-*Dimethylphenanthrene*.—γ-(6 : 7-*Dimethyl*-2-*naphthyl*)*butyric acid*, obtained in 90% yield from the corresponding keto-acid (J., 1932, 2250), crystallised from methyl alcohol in colourless prisms, m. p. 137—139° (Found: equiv., 241. $C_{16}H_{18}O_2$ requires equiv., 242). 4-*Keto*-6 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, obtained in 80% yield, crystallised from light petroleum (b. p. 60—80°) in stout colourless prisms, m. p. 112—113° (Found: C, 85·9; H, 7·4%). 2 : 3-*Dimethylphenanthrene*, obtained in 60% yield, crystallised from alcohol in glistening needles, m. p. 65—66° (Found: C, 92·9; H, 7·0%). The *picrate*, orange-red needles, m. p. 138—140°, from alcohol (Found: C, 61·0; H, 4·2%), *styphnate*, slender orange needles, m. p. 165—167°, from alcohol (Found: C, 58·5; H, 3·8%), *quinone*, orange-red prisms, m. p. 234—235°, from acetic acid (Found: C, 81·2; H, 5·0%), and *quinoxaline*, slender yellow prisms, m. p. 205°, from acetic acid (Found: N, 9·2%), were prepared.

2 : 4-*Dimethylphenanthrene*.—2-Naphthyl ethyl ketone, m. p. 56—58° (compare Rousset, *Bull. Soc. chim.*, 1896, **15**, 58), obtained in 95% yield by the action of ethylmagnesium iodide

(1·5 mols.) on β-naphthonitrile in toluene solution, was converted almost quantitatively into *2-naphthyl β-bromoethyl ketone*, which crystallised from light petroleum (b. p. 40—60°) in colourless plates, m. p. 81° (Found : Br, 30·1. $C_{13}H_{11}OBr$ requires Br, 30·4%) This reacted with ethyl sodiomalonate in the usual manner, giving a 70% yield of β-(2-naphthoyl)butyric acid, which would not crystallise. The crude keto-acid was converted in 25% yield into *4-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene*, which separated from methyl alcohol in colourless prisms, m. p. 79—80° (Found : C, 85·5; H, 6·7%). 2 : 4-Dimethyl-1 : 2-dihydrophenanthrene, b. p. 185—190°/10 mm., obtained in 95% yield by the action of methylmagnesium iodide on the cyclic ketone, was converted in 75% yield into *2 : 4-dimethylphenanthrene*, which crystallised from alcohol in colourless plates, m. p. 111° (Found : C, 93·2; H, 6·9%). The *picrate*, orange needles, m. p. 138—139°, from methyl alcohol (Found : C, 60·8; H, 3·6%), *quinone*, red plates, m. p. 169°, from methyl alcohol (Found : C, 80·9; H, 5·1%), and quinoxaline, cream needles, m. p. 155—156°, from acetic acid–chloroform (Found : C, 85·3; H, 5·1%), were prepared.

2 : 5-Dimethylphenanthrene.—This hydrocarbon, b. p. 204—205°/15 mm., obtained in 50% yield by dehydrogenation of the product of the reaction between methylmagnesium iodide and 4-keto-7-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene * (J., 1932, 1788), crystallised from alcohol in glistening prisms, m. p. 46—47° (Found : C, 93·4; H, 6·7%). The *picrate*, yellow needles, m. p. 127—129°, from alcohol (Found : C, 60·3; H, 3·8%), *styphnate*, orange needles, m. p. 132—133°, from alcohol (Found : C, 58·3; H, 3·6%), *quinone*, stout orange prisms, m. p. 140—141°, from acetic acid (Found : C, 81·4; H, 5·4%), and *quinoxaline*, slender yellow prisms, m. p. 166°, from acetic acid (Found : N, 9·3%), were prepared.

2 : 6-Dimethylphenanthrene.—β-(6-Methyl-2-naphthoyl)*iso*butyric acid (J., 1932, 2250) was reduced in 70% yield to γ-(6-methyl-2-naphthyl)-α-methylbutyric acid, which, without purification, was converted in 60% yield into 4-keto-3 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, an oil, b. p. 218—220°/20 mm., which gave a *semicarbazone*, crystallising from alcohol in small needles, m. p. 220—221° (Found : N, 15·1. $C_{17}H_{19}ON_3$ requires N, 14·9%). The cyclic ketone was converted in 60% yield into *2 : 6-dimethylphenanthrene*, which crystallised from methyl alcohol in colourless plates, m. p. 33—34° (Found : C, 93·0; H, 6·9%). The *picrate*, yellow needles, m. p. 135—136°, from methyl alcohol (Found : C, 61·0; H, 4·0%), styphnate, yellow needles, m. p. 148—150°, from methyl alcohol, *quinone*, orange needles, m. p. 202°, from acetic acid (Found : C, 81·8; H, 5·3%), and *quinoxaline*, pale yellow needles, m. p. 178—180°, from acetic acid (Found : N, 9·4%), were prepared.

2 : 7-Dimethylphenanthrene.—γ-(6-Methyl-2-naphthyl)-β-methylbutyric acid, obtained from the corresponding keto-acid (J., 1932, 2249) in 70% yield, was converted without purification in 50% yield into *4-keto-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene*, which separated from acetone in stout colourless prisms, m. p. 133—134° (Found : C, 85·6; H, 7·1%). *2 : 7-Dimethylphenanthrene* crystallised from methyl alcohol in colourless plates, m. p. 101—102° (Found : C, 93·1; H, 6·8%). The *picrate*, orange needles, m. p. 152—153°, from alcohol (Found : C, 60·4; H, 3·7%), *quinone*, orange plates, m. p. 224—225°, from alcohol (Found : C, 81·6; H, 5·1%) (compare Liebermann, *Ber.*, 1911, **44**, 1453, who gives 224°), and *quinoxaline*, cream needles, m. p. 235°, from acetic acid (Found : N, 8·9%), were prepared.

2 : 9-Dimethylphenanthrene [with J. MUSGRAVE].—β-(*4-Methyl-1-naphthoyl*)iso*butyric acid*, obtained in 75% yield by condensing methylsuccinic anhydride with 1-methylnaphthalene, crystallised from acetic acid in colourless plates, m. p. 141—142° (Found : equiv., 259. $C_{16}H_{16}O_3$ requires equiv., 256). The structure of this acid was established (a) by oxidation with sodium hypochlorite to 4-methyl-1-naphthoic acid and (b) by an independent synthesis from 4-methyl-1-naphthyl bromomethyl ketone and ethyl sodiomethylmalonate. The keto-acid was converted in 75% yield into γ-(4-methyl-1-naphthyl)-α-methylbutyric acid, which gave an 85% yield of *1-keto-2 : 9-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene*, crystallising from light petroleum (b. p. 60—80°) in colourless nodules, m. p. 84—85° (Found : C, 85·8; H, 7·2%). *2 : 9-Dimethylphenanthrene* crystallised from alcohol in colourless plates, m. p. 56—57° (Found : C, 92·8; H, 7·0%), and its *picrate* in long yellow needles, m. p. 138° (Found : C, 61·0; H, 3·9%).

3 : 4-Dimethylphenanthrene.—3 : 4-Dimethyl-1 : 2-dihydrophenanthrene, b. p. 192—194°/10 mm., obtained from methylmagnesium iodide and 4-keto-3-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (J., 1932, 1132), was converted in 80% yield into *3 : 4-dimethylphenanthrene*, which crystallised from methyl alcohol in colourless needles, m. p. 62—63° (Found : C, 93·0; H, 6·9%). The *picrate*, orange-red needles, m. p. 129—130°, from alcohol (Found : C, 60·5;

* The m. p. of γ-(6-methyl-2-naphthyl)butyric acid is 131—132° and not 111—112° as recorded in J., 1932, 1788. Our thanks are due to Dr. J. W. Cook for pointing out this mistake.

H, 4·0%), *styphnate*, orange-red needles, m. p. 142—143°, from alcohol (Found : C, 58·3; H, 3·9%), *quinone*, orange needles, m. p. 207—208°, from alcohol (Found : C, 80·7; H, 4·7%), and *quinoxaline*, pale yellow needles, m. p. 203—204°, from acetic acid (Found : N, 9·3%), were prepared.

3 : 6-*Dimethylphenanthrene.*—*Ethyl* 2-(β-p-*tolylethyl*)-5-*methyl*cyclo*hexanone*-2-*carboxylate*, obtained in 50% yield from β-*p*-tolylethyl bromide and ethyl 5-methyl*cyclo*hexanone-2-carboxylate, was an oil, b. p. 170—173°/0·4 mm. (Found : C, 75·5; H, 8·5%). This was twice reduced with 4% sodium amalgam, the product, b. p. 170—175°/0·4 mm. (yield, 30%), cyclised with phosphoric oxide, and the viscous oil, b. p. 160—170°/0·2 mm. (yield, 70%), converted into 3 : 6-*dimethylphenanthrene*, which crystallised from alcohol in colourless plates, m. p. 141° (Found : C, 92·8; H, 7·0%). The *picrate*, orange-yellow needles, m. p. 172—173°, from methyl alcohol (Found : C, 60·6; H, 3·9%), *quinone*, slender orange needles, m. p. 212—213°, from methyl alcohol (Found : C, 81·2; H, 5·0%), and *quinoxaline*, cream needles, m. p. 252°, from acetic acid–chloroform (Found : C, 85·6; H, 5·3%), were prepared.

1-*Ethylphenanthrene*, obtained in 60% yield by the action of ethylmagnesium iodide on 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene, followed by dehydration with formic acid, and dehydrogenation, crystallised from alcohol in colourless prisms, m. p. 62·5° (Found : C, 93·0; H, 7·0%). The *picrate*, slender orange prisms, m. p. 108—109°, from alcohol (Found : C, 60·7; H, 4·0%), *styphnate*, yellow needles, m. p. 144°, from alcohol (Found : C, 58·8; H, 4·0%), *quinone*, orange prisms, m. p. 155°, from acetic acid (Found : C, 81·9; H, 5·1%), and *quinoxaline*, slender cream needles, m. p. 151°, from acetic acid (Found : N, 8·9%), were prepared. Pschorr (*loc. cit.*) and Gadamer (*loc. cit.*) give 109—110°, 138—140°, and 187—188° for the m. p.'s of the hydrocarbon, its picrate, and quinone respectively. 1-Ethylphenanthrene was oxidised by means of alkaline potassium ferricyanide to phenanthrene-1-carboxylic acid, m. p. 232°, the methyl ester, m. p. 56°, of which was also prepared (Fieser, *J. Amer. Chem. Soc.*, 1929, **51**, 2460).

1-iso*Propylphenanthrene*, obtained similarly in 50% yield from *iso*propylmagnesium iodide, crystallised from alcohol in colourless prisms, m. p. 85—86° (Found : C, 93·0; H, 7·4. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%). The *picrate*, yellow needles, m. p. 125—126°, from methyl alcohol (Found : C, 61·4; H, 4·4. $C_{23}H_{19}O_7N_3$ requires C, 61·4; H, 4·2%), *quinone*, orange plates, m. p. 147—148°, from alcohol (Found : C, 81·5; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%), and *quinoxaline*, cream needles, m. p. 142—143°, from acetic acid–chloroform (Found : N, 9·1. $C_{23}H_{18}N_2$ requires N, 9·1%), were prepared.

1-*Propylphenanthrene*, obtained similarly in 45% yield from propylmagnesium iodide, crystallised from methyl alcohol in colourless plates, m. p. 34—35° (Found : C, 92·5; H, 7·1%). The *picrate*, yellow needles, m. p. 100—101°, from methyl alcohol (Found : C, 61·2; H, 4·2%), *quinone*, orange plates, m. p. 139—140°, from alcohol (Found : C, 81·2; H, 5·4%), and *quinoxaline*, pale yellow needles, m. p. 144—145°, from acetic acid (Found : N, 9·0%), were prepared.

2-iso*Propylphenanthrene.*—Crude γ-(6-*iso*propyl-2-naphthyl)butyric acid, obtained in 60% yield from the corresponding keto-acid (J., 1932, 1790), was converted in 75% yield into 4-*keto*-7-iso*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, which crystallised from light petroleum (b. p. 40—45°) in colourless prisms, m. p. 55—56° (Found : C, 85·5; H, 7·7. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%). 2-iso*Propylphenanthrene*, obtained in 60% yield, crystallised from methyl alcohol in colourless prisms, m. p. 44—45° (Found : C, 92·4; H, 7·2%). The *picrate*, pale yellow needles, m. p. 108°, from methyl alcohol (Found : C, 61·3; H, 4·2%), *quinone*, orange plates, m. p. 134°, from methyl alcohol (Found : C, 81·3; H, 5·5%), and *quinoxaline*, pale cream needles, m. p. 172°, from acetic acid (Found : N, 8·8%), were prepared.

2-*Methyl*-1-*ethylphenanthrene.*—2-*Methyl*-1-*ethyl*-3 : 4-*dihydrophenanthrene*, obtained in 90% yield from ethylmagnesium iodide and 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (J., 1932, 1132), crystallised from alcohol in colourless plates, m. p. 77—78° (Found : C, 91·8, H, 8·3. $C_{17}H_{18}$ requires C, 91·9; H, 8·1%). The picrate separated in scarlet needles which dissociated on attempted recrystallisation from alcohol. 2-*Methyl*-1-*ethylphenanthrene* crystallised from methyl alcohol in colourless plates, m. p. 80° (Found : C, 92·6; H, 7·4%). The *picrate*, yellow needles, m. p. 134—135°, from methyl alcohol (Found : C, 61·5; H, 4·2%), *quinone*, red needles, m. p. 157—159°, from acetic acid (Found : C, 81·4; H, 5·7%), and *quinoxaline*, cream needles, m. p. 146—147°, from acetic acid (Found : N, 9·0%), were prepared.

1-*Methyl*-2-*ethylphenanthrene.*—β-(1-*Naphthoyl*)-α-*ethylpropionic acid*, obtained in 60% yield from ethyl sodioethylmalonate and 1-naphthyl bromomethyl ketone, crystallised from benzene–light petroleum (b. p. 60—80°) in colourless prisms, m. p. 112—113° (Found : equiv., 259. $C_{16}H_{16}O_3$ requires equiv., 256). This was reduced and the oily product converted in

60% yield (calc. on the keto-acid used) into 1-*keto*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, which crystallised from light petroleum (b. p. 60—80°) in colourless plates, m. p. 60—61° (Found : C, 85·6; H, 7·2%). 1-Methyl-2-ethyl-3 : 4-dihydrophenanthrene, a solid obtained in 95% yield by the action of methylmagnesium iodide on the cyclic ketone, was converted, without purification, into 1-*methyl*-2-*ethylphenanthrene*, which crystallised from alcohol in colourless plates, m. p. 100° (Found : C, 92·4; H, 7·3%). The *picrate*, yellow needles, m. p. 134—135°, from methyl alcohol (Found : C, 61·7; H, 4·1%), *quinone*, orange plates, m. p. 163°, from alcohol (Found : C, 81·5; H, 5·4%), and *quinoxaline*, cream needles, m. p. 108°, from acetic acid–chloroform (Found : C, 85·5; H, 5·8%), were prepared.

Our thanks are due to the Research Fund Committee of the Chemical Society for a grant, and to the Council of Armstrong College for a studentship which has enabled one of us (C. R. M.) to participate in this work.

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[*Received, February 2nd*, 1934.]