60. *Polycyclic Aromatic Hydrocarbons. Part XXII.*

By C. L. Hewett.

1 : 2-Dimethylchrysene has been obtained by an adaptation of the Pschorr synthesis of phenanthrene derivatives and also by the action of methylmagnesium iodide on chrysaquinone.

In the course of unsuccessful attempts to synthesise 1 : 2 : 3 : 4-tetramethylphenanthrene, 1 : 2 : 3 : 4-*tetramethylanthracene* was obtained.

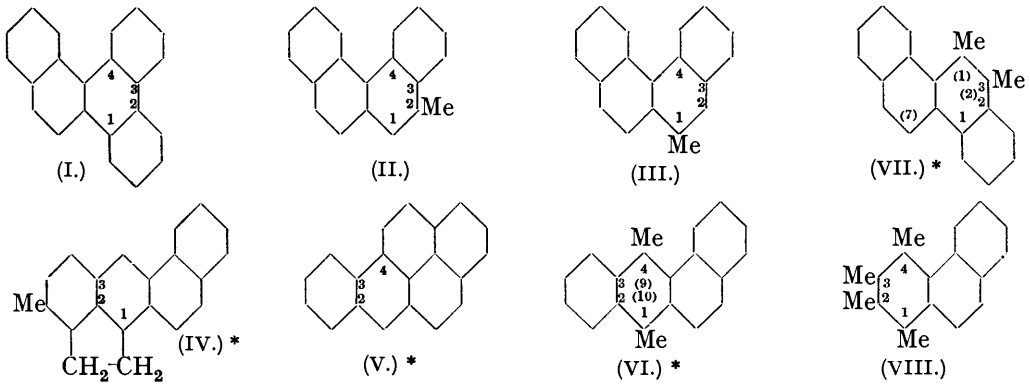
1-*Methyl*-3 : 4-*benzphenanthrene* (III) has been obtained by indirect reduction of 3 : 4-benz-1-phenanthroic acid, and a new route to 2-substituted 3 : 4-benzphenanthrenes, for example, 2-iso*propyl*-3 : 4-*benzphenanthrene*, has been devised.

The weakly carcinogenic properties of 3 : 4-benzphenanthrene have been known for some time (Barry, Cook, Haslewood, Hewett, Hieger, and Kennaway, *Proc. Roy. Soc.*, 1933, *B*, **117**, 318) and the fairly high degree of carcinogenic activity shown by 2-methyl-3 : 4-benzphenanthrene (II) [Hewett, J., 1936, 596; Bachmann, Cook, Dansi, de Worms,

Haslewood, Hewett, and (Mrs.) Robinson, *Proc. Roy. Soc.*, 1937, *B*, **123**, 359] and 1 : 2 : 3 : 4-dibenzphenanthrene (I) (Hewett, J., 1938, 193; unpublished experiments) indicates that this activity is in fact an inherent property of the 3 : 4-benzphenanthrene molecule. These derivatives of 3 : 4-benzphenanthrene, unlike those of 1 : 2-benzanthracene, produce a form of new growth in the liver, and possibly other tumours as well.

Substitution in either or both of the 1- and the 2-position of the molecule seems necessary to bring about the increased carcinogenic activity shown by 2-methyl-3 : 4-benzphenanthrene and 1 : 2 : 3 : 4-dibenzphenanthrene, for as yet, after one year, fewer tumours have been obtained with the 6-, 7- and 8-methyl derivatives of 3 : 4-benzphenanthrene (Hewett, J., 1938, 1286) either by application in benzene solution to the skin of mice or by injection. 1 : 2 : 5 : 6-Dibenzphenanthrene (Hewett, *loc. cit.*) also has only weakly carcinogenic activity, comparable with that of the parent hydrocarbon, 3 : 4-benzphenanthrene, itself. 6 : 7-Dimethyl-3 : 4-benzphenanthrene (Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1936, **58**, 1463) has been reported to be without carcinogenic activity after being applied to mice for 16 months (see Newman and Joshel, *ibid.*, 1938, **60**, 486). 1-Methyl-3 : 4-benzphenanthrene (III) (this paper), on the other hand, has produced four epitheliomas and two papillomas in a series of 20 mice in a period of 335 days.

Of the three tetracyclic aromatic hydrocarbons, chrysene (1 : 2-benzphenanthrene), 1 : 2-benzanthracene (2 : 3-benzphenanthrene), and 3 : 4-benzphenanthrene, only the last has carcinogenic activity to any marked degree. These three hydrocarbons are all derivatives of phenanthrene each substituted in two of the 1-, 2-, 3- and 4-positions. Further substitution of 2 : 3-benzphenanthrene (1 : 2-benzanthracene) in either or both of the remaining 1- and 4-positions gives rise to highly carcinogenic hydrocarbons [*e.g.*, methylcholanthrene (IV), Bachmann *et al.*, *loc. cit.*; 3 : 4-benzpyrene (V), Barry *et al.*, *loc. cit.*; 9 : 10-dimethyl-1 : 2-benzanthracene (VI), Bachmann, Kennaway, and Kennaway, *Yale J. Biol. Med.*, 1938, **11**, 97]. Moreover, further substitution of the 3 : 4-benzphenanthrene molecule in the 1- or the 2-positions or in both leads to enhanced activity. In each of these cases, the active compound is a phenanthrene derivative substituted in at least three of the positions 1, 2, 3 and 4. It thus seemed probable that, if the 3- and the 4-position of 1 : 2-benzphenanthrene (chrysene) were substituted by methyl groups, again giving a phenanthrene substituted in all of the positions 1, 2, 3 and 4, a carcinogenic chrysene derivative could be obtained. This has proved to be the case; 1 : 2-*dimethylchrysene* (VII) has now been prepared and is undergoing biological test. In an experiment of which the present duration is 389 days, four epitheliomas have been obtained in 20 mice.



In the hydrocarbons under discussion, disubstitution in the 1-, 2-, 3- and 4-positions of phenanthrene leads to little or no activity, whereas tri- or tetra-substitution leads to marked activity. This substitution may be either by two benzene rings (I) or by one benzene ring and one or two methyl groups (II, III, IV, VI, VII), activity being retained

* The numbering given in these formulæ indicates their structural relation to phenanthrene rather than to anthracene or chrysene. In formulæ (VI) and (VII) the official anthracene and chrysene numbering is given in parentheses.

whatever positions the benzene ring occupies. The fact that the benzene ring and methyl groups may be interchanged without loss of activity makes it desirable to obtain 1 : 2 : 3 : 4-tetramethylphenanthrene (VIII), in which all four of the positions in question are occupied by methyl groups. Should this compound prove to be active, it would represent a carcinogenic prototype of each of the three aromatic tetracyclic hydrocarbons. An attempt to prepare it led to 1 : 2 : 3 : 4-*tetramethylanthracene* (XVII).

In order to study the effect on carcinogenic activity of the size of the substituent in the 2-position of the 3 : 4-benzphenanthrene molecule, 2-iso*propyl*-3 : 4-*benzphenanthrene* has been prepared. It is as yet too early to assess its activity, but after 12 months four epitheliomas have been obtained in a series of 20 mice.

1-Methyl-3 : 4-benzphenanthrene was readily obtained by the Kishner–Wolff reduction of 3 : 4-*benz*-1-*phenanthraldehyde*, which was prepared from the anilide of 3 : 4-benz-1-phenanthroic acid (Hewett, J., 1938, 1286) by reduction of the iminochloride with stannous chloride.

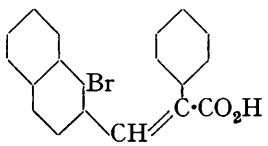
1-Bromo-2-naphthaldehyde, prepared in poor yield by Mayer and Sieglitz (*Ber.*, 1922, **55**, 1859) from 1-bromo-2-bromomethylnaphthalene and hexamine, in boiling aqueous alcoholic solution, is obtained in good yield when the solvent is boiling acetic acid. The condensation with sodium phenylacetate and acetic anhydride gave α-*phenyl*-β-2-(1-*bromonaphthyl*)*acrylic acid* (IX), which underwent cyclisation with fused potash to give an excellent yield of 3 : 4-*benz*-2-*phenanthroic acid* (X).

An attempt to prepare 1 : 2-*dihydro*-3 : 4-*benz*-1-*phenanthroic acid* by the cyclisation of α-2-(1-*bromonaphthyl*)-β-*phenylpropionic acid* by means of fused potash gave poor results. A small amount of 3 : 4-benz-1-phenanthroic acid and also of the dihydro-acid was obtained, but the main product was α-2-(1-*hydroxynaphthyl*)-β-*phenylpropionic acid*. Fieser, Joshel, and Seligman (*J. Amer. Chem. Soc.*, 1939, **61**, 2134), endeavouring to prepare a methylchrysene by cyclisation, with fused potassium hydroxide, of 1-(*o*-chlorophenyl)-2-(α-naphthyl)propene, obtained only tar. The success of the reaction in the preparation of the benzphenanthroic acids is probably associated with the configuration of the acids obtained by the Perkin condensation, which usually have the *cis*-configuration.

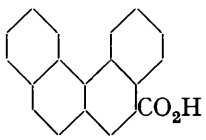
Methyl 3 : 4-*benz*-2-*phenanthroate* (from X) reacted with methylmagnesium iodide to give a *carbinol*, which was readily dehydrated with picric acid to 2-iso*propenyl*-3 : 4-*benzphenanthrene*. Hydrogenation of this unsaturated compound with a palladium catalyst gave 2-*iso*propyl-3 : 4-benzphenanthrene.

1 : 2-Dimethylnaphthalene (Darzens and Lévy, *Compt. rend.*, 1936, **202**, 74) was brominated to give 1-*bromo*-3 : 4-*dimethylnaphthalene*, the structure of which was proved by conversion of the Grignard compound prepared from it into the known 1 : 2 : 4-trimethylnaphthalene (Ruzicka and Ehmann, *Helv. Chim. Acta*, 1932, **15**, 140). Chloromethylation also took place in the same position, for the chloromethyl compound obtained gave, on reduction, the same trimethylnaphthalene.

3 : 4-Dimethyl-1-naphthylmagnesium bromide reacted with ethylene oxide to give β-1-(3 : 4-*dimethylnaphthyl*)*ethyl alcohol*, which was readily converted into the *chloride* by means of thionyl chloride. The carbinol obtained from the Grignard reaction with this chloride and 2-methyl*cyclo*hexanone was heated with phosphoric oxide to give a gum, which resinified on heating with selenium.



(IX.)



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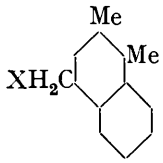
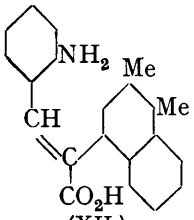


(XI.)

The chlorine atom in 1-*chloromethyl*-3 : 4-*dimethylnaphthalene* (XI; X = Cl) is very reactive (compare 10-chloromethyl-1 : 2-benzanthracene; Badger and Cook, J., 1939, 803) and in the preparation of the *nitrile* (XI; X = CN) by means of aqueous alcoholic potassium cyanide, a large amount of by-product was obtained, which was probably the

ethoxy-compound. The nitrile was best prepared by heating with cuprous cyanide in phenylacetonitrile solution.

The sodium salt of the 3 : 4-*dimethyl*-1-*naphthylacetic acid* (XI; X = CO_2H) obtained by hydrolysis of this nitrile was condensed with *o*-nitrobenzaldehyde, and the resulting *cinnamic acid* derivative reduced to the *amino-acid* (XII). Ring closure was brought about by the modified Pschorr reaction (Bogert and Stamatoff, *Rec. Trav. chim.*, 1933, **52**, 589). The 1 : 2-*dimethylchrysene*-7-*carboxylic acid* thus obtained was decarboxylated to 1 : 2-dimethylchrysene (VII).



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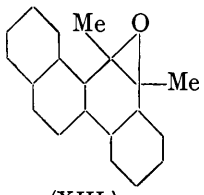

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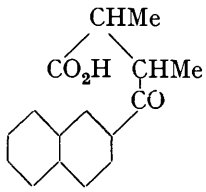

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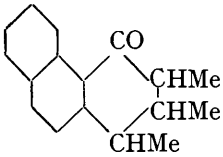

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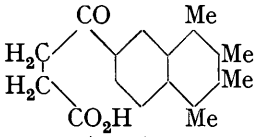

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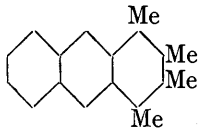

(XVII.)

The *diol* arising from the reaction between chrysaquinone and methylmagnesium iodide was converted into the *oxide* (XIII) by passing hydrogen chloride into its solution in methyl alcohol. Addition of hydriodic acid to a cold solution of the oxide in acetic acid gave a precipitate of an unstable iodo-compound, which was reduced by zinc dust and alcohol, in rather poor yield, to 1 : 2-dimethylchrysene.

1 : 2-Dimethylchrysene-1 : 2-oxide was hydrogenated with a platinum catalyst in hot acetic acid directly to the aromatic hydrocarbon, but the yield was poor and uncertain. However, by using a palladium catalyst and acetone as a solvent, an almost quantitative yield of 1 : 2-*dihydro*-1 : 2-*dimethylchrysene* was obtained; this was readily dehydrogenated to the aromatic hydrocarbon with platinum.

An attempt to synthesise 1 : 2 : 3 : 4-tetramethylphenanthrene involved the building of a new ring on to a naphthalene molecule with progressive introduction of new methyl groups. 2-α-*Bromopropionylnaphthalene* was condensed with ethyl sodiomethylmalonate; the product after hydrolysis and decarboxylation gave β-2-*naphthoyl*-αβ-*dimethylpropionic acid* (XIV). The methyl ester of this acid with methylmagnesium iodide gave a *lactone*, which was reduced to γ-2-*naphthyl*-αβγ-*trimethylbutyric acid*; this gave an oily ketone (XV) on ring closure. The carbinol arising from this ketone and methylmagnesium iodide, after dehydration, was heated with palladium to give a mixture which could not be purified.

In an endeavour to overcome any possibility of losing a methyl group from a hydrogenated ring, 1 : 2 : 3 : 4-*tetramethylnaphthalene* was employed as starting material, since all the methyl groups in the final dehydrogenation would be already in an aromatic ring. 2 : 3-Dimethylnaphthalene was chloromethylated, and the product hydrogenated to 1 : 2 : 3-trimethylnaphthalene (Ruzicka and Ehmann, *loc. cit.*), which on further chloromethylation and hydrogenation gave 1 : 2 : 3 : 4-tetramethylnaphthalene, the structure of which was established by the isolation of methyl mellitate from the methyl esters of the acids obtained by oxidation with dilute nitric acid. 1 : 2 : 3 : 4-Tetramethylnaphthalene underwent the Friedel–Crafts reaction with succinic anhydride to give a single *acid* (XVI), which was shown to be the 6-isomeride. The *ketone* obtained by ring closure, with 80% sulphuric acid, of the *acid* obtained by Clemmensen reduction was reduced by the Kishner–Wolff method to a *tetrahydro*-compound, which became dehydrogenated with difficulty to 1 : 2 : 3 : 4-tetramethylanthracene (XVII). The structure of this hydrocarbon as an

anthracene was shown by its behaviour towards maleic anhydride, with which it readily reacted in boiling xylene, giving an *adduct* from which the original hydrocarbon was regenerated by sublimation at 300°. On oxidation 1 : 2 : 3 : 4-tetramethylanthracene gave a p-*quinone*.

The formation of an anthracene derivative in the aforementioned ring-closure, in preference to a phenanthrene derivative, is a striking example of the hindering effect of an α-methyl group. This effect has also been observed by Haworth and Sheldrick (J., 1934, 1950), who obtained 5-keto-1-methyl-5 : 6 : 7 : 8-tetrahydroanthracene on ring closure of γ-7-(1-methylnaphthyl)butyric acid. In this present instance the effect of the α-methyl group is even more pronounced, as, although there are two α-positions in the naphthalene nucleus vacant, both the original condensation and the subsequent cyclisation occurred in the β-positions.

EXPERIMENTAL.

1-*Methyl*-3 : 4-*benzphenanthrene* (III).—3 : 4-Benz-1-phenanthroic acid (18 g.) was refluxed with thionyl chloride (75 c.c.) for 1 hour, and the excess removed under reduced pressure. The *anilide*, prepared from this acid chloride and aniline (2 mols.), crystallised from xylene in colourless plates (18 g.), m. p. 215—216° (Found : C, 85·9; H, 5·6; N, 3·9. $C_{25}H_{17}ON$ requires C, 86·4; H, 4·9; N, 4·0%). The anilide (14 g.) was dissolved in tetrachloroethane (60 c.c.) and heated with phosphorus pentachloride (11·5 g.) at 150° for ½ hour. The phosphorus oxychloride and the solvent were then removed, and the residual iminochloride redissolved in fresh tetrachloroethane (20 c.c.) and slowly added to a solution of stannous chloride (42 g.) in ether (375 c.c.) saturated with hydrogen chloride, cooled in ice. After 18 hours at 2—3°, the ether and tetrachloroethane were distilled off with steam, and the residue hydrolysed with hydrochloric acid. The product was distilled, the fraction, b. p. 235—236°/0·2 mm., being collected (6·8 g.). The resulting 3 : 4-*benz*-1-*phenanthraldehyde* crystallised from alcohol in yellow plates, m. p. 81—82° (Found : C, 88·6; H, 4·4. $C_{19}H_{12}O$ requires C, 89·0; H, 4·7%). The *semicarbazone*, prepared in alcoholic solution, had m. p. 220—222° (Found : N, 13·0. $C_{20}H_{15}ON_3$ requires N, 13·4%).

The semicarbazone (6·2 g.) was heated with sodium ethoxide (sodium, 6·2 g., in ethyl alcohol, 90 c.c.) in sealed tubes at 180° for 16 hours. The product was distilled at 200—210°/0·4 mm., and the distillate (3 g.) converted into the *picrate*, which crystallised from alcohol in vermilion needles, m. p. 112·5—113·5° (Found : C, 64·0; H, 3·7. $C_{19}H_{14},C_6H_3O_7N_3$ requires C, 63·7; H, 3·6%). 1-*Methyl*-3 : 4-*benzphenanthrene* was regenerated from the picrate by passage of its benzene solution through a column of alumina, and the hydrocarbon was distilled from an air-bath at 210°/0·4 mm.; it formed a solid which crystallised from alcohol in colourless cubes, m. p. 77—78° (Found : C, 94·3; H, 5·8. $C_{19}H_{14}$ requires C, 94·0; H, 6·0%).

2-iso*Propyl*-3 : 4-*benzphenanthrene*.—1-*Bromo*-2-*naphthaldehyde* (cf. Mayer and Sieglitz, *loc. cit.*). 1-Bromo-2-bromomethylnaphthalene (50 g.) was dissolved in boiling acetic acid (100 c.c.), finely powdered hexamine (25 g.) added, and the whole heated over a naked flame until the solution became clear (about 30 seconds). Water (75 c.c.) was then added, and the aldehyde allowed to crystallise. Recrystallisation from acetic acid gave pure 1-bromo-2-naphthaldehyde, m. p. 117—118°. Yield, 210 g. from 680 g. of the dibromo-compound.

α-*Phenyl*-β-2-(1-*bromonaphthyl*)*acrylic acid* (IX). 1-Bromo-2-naphthaldehyde (69 g.), sodium phenylacetate (72 g.), and acetic anhydride (280 c.c.) were heated on a water-bath for 24 hours, water added, and heating continued until all the acetic anhydride had decomposed. The solid acid was purified through its ammonium salt. The pure *acid* crystallised from acetic acid in colourless plates, m. p. 211—212° (Found : C, 64·55; H, 3·8. $C_{19}H_{13}O_2Br$ requires C, 64·6; H, 3·7%). In this way 233 g. of acid were prepared from 215 g. of aldehyde. In an experiment carried out at 130° for 6 hours, the yield was 10% less.

3 : 4-*Benz*-2-*phenanthroic acid* (X). The foregoing acid (10 g.) and potassium hydroxide (40 g.) were heated in an oil-bath at 260° for 10 minutes. During the vigorous reaction which took place, the vessel was removed from the bath and replaced when this had subsided. A slightly higher temperature was needed for the ring closure of this acid than for the corresponding 1-isomer described in Part XVIII (J., 1938, 1288). The 3 : 4-*benz*-2-*phenanthroic acid* was purified through its sparingly soluble sodium salt, which separated in colourless plates. After crystallisation from acetic acid, the free acid formed pale yellow needles, m. p. 236—237° (Found : C, 83·85; H, 4·6. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·45%). Yield, 115 g. from 233 g. of the bromo-acid.

Methyl 3 : 4-*benz*-2-*phenanthroate* (10·7 g.), prepared from the acid (10 g.) by methyl-alcoholic hydrogen chloride, crystallised from light petroleum (b. p. 80—100°) in colourless plates, m. p. 76—77° (Found : C, 83·9; H, 5·0. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%).

The methyl ester (4 g.) was added to methylmagnesium iodide prepared from methyl iodide (8·0 g.), magnesium (1·4 g.), and ether (25 c.c.) cooled in ice. The whole was refluxed on the water-bath for 1 hour and decomposed with ice and ammonium chloride. After removal of the ether from the washed and dried solution, the residue was recrystallised from alcohol, 3 : 4-*benz*-2-*phenanthryldimethylcarbinol* being obtained in colourless micro-needles, m. p. 139—140° (Found : C, 87·7; H, 6·3. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%). The liquors consisted mainly of the unsaturated hydrocarbon. In another experiment, the crude carbinol arising from 5·2 g. of methyl ester was refluxed in alcohol with picric acid for 1 hour, and the *picrate* (9·8 g.) of 2-iso*propenyl*-3 : 4-*benzphenanthrene* separated on cooling. After recrystallisation from alcohol it formed vermilion needles, m. p. 113—113·5° (Found : C, 65·4; H, 4·3. $C_{21}H_{16},C_6H_3O_7N_3$ requires C, 65·15; H, 3·9%). The *iso*propenyl compound, regenerated from the picrate by passage of the benzene solution through alumina, was hydrogenated in alcoholic solution with a palladium catalyst. The resulting 2-iso*propyl*-3 : 4-*benzphenanthrene* was purified through its *picrate*, which crystallised from alcohol in vermilion needles, m. p. 116·5—117° (Found : C, 65·2; H, 4·5. $C_{21}H_{18},C_6H_3O_7N_3$ requires C, 64·9; H, 4·25%). The regenerated hydrocarbon crystallised from alcohol in colourless plates, m. p. 91·5—92·5° (Found : C, 93·5; H, 6·8. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%).

1 : 2-*Dihydro*-3 : 4-*benz*-1-*phenanthroic Acid*.—Ethyl 1-bromo-2-naphthylacetate (100 g.) was added to a solution of sodium ethoxide, prepared from sodium (8·75 g.) and alcohol (35 c.c.), in ether (400 c.c.) containing ethyl oxalate (66 g.). After being kept for 16 hours at room temperature and 2 hours at the b. p., the mixture was poured on ice and sulphuric acid, and the ethereal layer washed and dried (cf. Wislicenus, *Ber.*, 1894, **27**, 1092). The residue from the evaporation of the ether was pyrolysed at 200—210°/20 mm. for ½ hour and then distilled. The redistilled *ethyl* 1-*bromo*-2-*naphthylmalonate* (110 g.) had b. p. 187—189°/0·3 mm. (Found : C, 56·3; H, 4·6. $C_{17}H_{17}O_4Br$ requires C, 55·9; H, 4·7%). The sodio-compound prepared from the foregoing ester (62 g.) and sodium (4·3 g.) in ethyl alcohol (150 c.c.) was treated with benzyl chloride (23·6 g.), and the whole heated on the water-bath for 5 hours. Potassium hydroxide (25 g.) in a small amount of water was then added, boiling continued, and the alcohol distilled off. After dilution with water and extraction with ether, the alkaline solution was acidified, and the malonic acid collected, dried, and decarboxylated. The product was a mixture of acids and was purified by distillation of the methyl esters, the fraction, b. p. 210—220°/0·4 mm., being collected. Hydrolysis gave α-2-(1-*bromonaphthyl*)-β-*phenylpropionic acid*, which crystallised from acetic acid in colourless plates, m. p. 131—132° (Found : C, 64·5; H, 4·3. $C_{19}H_{15}O_2Br$ requires C, 64·2; H, 4·25%).

Ring closure. The foregoing acid (4·5 g.) was dissolved in quinoline (45 c.c.) and heated at 250—260° with potassium hydroxide (22·5 g.) for 2 hours. The product was distilled at 210°/0·3 mm. (2·9 g.). This was α-*phenyl*-β-2-(1-*bromonaphthyl*)*ethane* (Found : C, 69·9; H, 5·0. $C_{18}H_{15}Br$ requires C, 69·4; H, 4·9%).

The acid (10 g.) was heated with potassium hydroxide (50 g.) at 260° for 15 minutes and the crude mixture of acids obtained by acidifying the aqueous solution was converted into the ethyl esters and distilled. Three fractions were collected: (i) b. p. 180°/0·4 mm., (ii) b. p. 180—187°/0·4 mm., (iii) b. p. 200—210°/0·4 mm. Fraction (i) on hydrolysis gave 1 : 2-*dihydro*-3 : 4-*benz*-1-*phenanthroic acid*, which crystallised from benzene in colourless plates, m. p. 140·5—141·5° (Found : C, 82·7; H, 5·8. $C_{19}H_{14}O_2$ requires C, 83·15; H, 5·15%). Yield, 0·3 g. Fraction (ii) on hydrolysis gave β-*phenyl*-α-2-(1-*hydroxynaphthyl*)*propionic acid*, which formed plates from benzene, m. p. 146·5—147·5° (Found : C, 77·5; H, 5·55. $C_{19}H_{16}O_3$ requires C, 78·0; H, 5·5%). The third fraction on hydrolysis gave 3 : 4-benz-1-phenanthroic acid, m. p. 240—242°, not depressed by an authentic specimen.

1 : 2-*Dimethylchrysene*.—(i) 1-*Bromo*-3 : 4-*dimethylnaphthalene*. 1-Chloromethyl-2-methylnaphthalene (Darzens and Lévy, *loc. cit.*) (50 g.) in alcohol (160 c.c.) and water (40 c.c.) was heated on the water-bath with zinc dust (65 g.) (Zelinsky, *Ber.*, 1901, **34**, 2801). A violent reaction immediately set in, which was moderated by plunging the flask into a freezing mixture; after the reaction had subsided, the reaction mixture was refluxed on the water-bath for 1 hour. The zinc dust was filtered off and extracted several times with hot alcohol, and the alcoholic extracts evaporated to small bulk. The residue was extracted with ether and washed, dried, and evaporated. The 1 : 2-dimethylnaphthalene was distilled, b. p. 135—136°/14 mm. (26 g.). The less volatile residue consisted of as.-1 : 1′-(2 : 2′-*dimethyldinaphthyl*)*ethane*, which, recrystal-

lised from toluene, formed fine colourless plates, m. p. 177—178° (Found: C, 92·6; H, 7·0. $C_{24}H_{22}$ requires C, 92·85; H, 7·15%). A further quantity of this material was obtained from the zinc residues by extraction with boiling toluene.

1 : 2-Dimethylnaphthalene (18 g.) was dissolved in carbon disulphide (50 c.c.), and bromine (5·8 c.c.) in carbon disulphide (10 c.c.) slowly added in the dark. After the bromine had all reacted, the pale straw-coloured liquid was evaporated, and the residue distilled, b. p. 190—195°/14 mm. (22·3 g.). The *picrate* separated from alcohol in yellowish-orange needles, m. p. 108—109° (Found: C, 47·2; H, 3·2. $C_{12}H_{11}Br,C_6H_3O_7N_3$ requires C, 46·5; H, 3·0%). 1-*Bromo*-3 : 4-*dimethylnaphthalene*, regenerated from the picrate, crystallised from light petroleum in colourless rhombs, m. p. 39—40° (Found: C, 61·4; H, 4·8. $C_{14}H_{11}Br$ requires C, 61·2; H, 4·7%).

A Grignard solution prepared from 1-bromo-3 : 4-dimethylnaphthalene (11·8 g.), magnesium (1·2 g.), and ether (25 c.c.) was treated, with ice cooling, with methyl sulphate (9·5 g.). After the reaction had subsided, the whole was boiled for 1 hour, decomposed with ice and dilute sulphuric acid, and the ethereal solution washed, dried, and evaporated. The residue on distillation gave 1 : 2 : 4-trimethylnaphthalene, b. p. 155—165°/18 mm., m. p. 50—51°, which gave a picrate, m. p. 145—147°, and a styphnate, m. p. 122—123° (Ruzicka and Ehmann, *loc. cit.*, give the m. p.'s 50°, 147·5°, and 123·5° respectively).

A Grignard solution prepared from the bromo-compound (63 g.), magnesium (6·6 g.), and ether (200 c.c.) was treated in ice with ethylene oxide (13·3 g.). After working up in the usual manner, the product was distilled, and the fraction, b. p. 150—152°/0·3 mm., collected (29 g.). Crystallisation from light petroleum and then from *cyclo*hexane gave colourless tablets of β-1-(3 : 4-*dimethylnaphthyl*)*ethyl alcohol*, m. p. 65° (Found: C, 83·9; H, 8·0. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). The *chloride*, prepared by means of thionyl chloride in the usual manner, had b. p. 140—145°/0·3 mm.; recrystallised from methyl alcohol, it formed colourless needles, m. p. 44—45° (Found: C, 76·7; H, 6·9. $C_{14}H_{15}Cl$ requires C, 76·8; H, 6·9%).

A Grignard solution prepared from the chloride (12·6 g.), magnesium (1·5 g.), and ether (40 c.c.) was treated with 2-methyl*cyclo*hexanone (6·9 g.) in ether (10 c.c.) with ice cooling. After ½ hour in ice and 2 hours' boiling, the product was decomposed with ammonium chloride and ice, and the residue from the evaporation of the ether distilled, b. p. 195—200°/0·5 mm. (8·3 g.). It was not possible to obtain this carbinol sufficiently pure for analysis, but when it (2·2 g.) was heated with phosphoric oxide (4·4 g.) at 160° for 1 hour, and the ether-extracted product heated with selenium, there was obtained only a very small amount of an oily brown distillate which could not be obtained crystalline.

1-*Chloromethyl*-3 : 4-*dimethylnaphthalene* (XI; X = Cl). In several attempts to chloromethylate 1 : 2-dimethylnaphthalene under various conditions, it was found that temperature had a great influence on the yield of chloromethyl compound and that the lower the temperature the less the amount of diarylmethane formed. For example, if the reaction was carried out according to Darzens and Lévy (*loc. cit.*) in a sealed bottle for 20 hours at 60°, the yield, from 15·2 g. of hydrocarbon, was 4·5 g.; at room temperature for 16 hours the yield reached its maximum of 11 g.; reaction at 0° for 48 hours gave a yield of 10 g. and unchanged material still remained. The following method was finally adopted: 1 : 2-Dimethylnaphthalene (68 g.) was dissolved in acetic acid (200 c.c.), paraformaldehyde (26·3 g.) added, and hydrogen chloride passed through until the paraformaldehyde passed into solution, the whole being cooled in ice. The mixture was then left at room temperature for 16 hours, diluted with water, and extracted with benzene. The benzene extract was washed with dilute sodium carbonate solution and evaporated; the residue was distilled, b. p. 143—145°/0·8 mm. 1-*Chloromethyl*-3 : 4-*dimethylnaphthalene*, recrystallised from light petroleum, formed colourless needles (46 g.), m. p. 70—71° (Found: C, 76·2; H, 6·4. $C_{13}H_{13}Cl$ requires C, 76·2; H, 6·4%). The residue from the distillation was recrystallised from benzene; it had m. p. 174—175° and analysis showed it to be 3 : 3′ : 4 : 4′-*tetramethyl*-1 : 1′-*dinaphthylmethane* (Found: C, 92·5; H, 7·5. $C_{25}H_{24}$ requires C, 92·5; H, 7·5%). 1-Chloromethyl-3 : 4-dimethylnaphthalene on reduction with zinc dust and aqueous alcohol as already described gave 1 : 2 : 4-trimethylnaphthalene, m. p. 49—50°; picrate, m. p. 146—147°.

3 : 4-*Dimethylnaphthyl*-1-*acetic acid* (XI; X = CO_2H). 1-Chloromethyl-3 : 4-dimethylnaphthalene (17·2 g.) was dissolved in alcohol (100 c.c.) and refluxed for 3 hours with potassium cyanide (8·4 g.) in water (10 c.c.), and the crude product hydrolysed with alcoholic potassium hydroxide. The resulting 3 : 4-*dimethyl*-1-*naphthylacetic acid* (5·1 g.) separated from acetic acid in colourless plates, m. p. 181—182° (Found: C, 78·3; H, 6·7. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%). The major part of the chloromethyl compound had been converted into a

neutral substance, which was not further investigated but was probably the ethoxymethyl compound similar to that obtained by Badger and Cook (*loc. cit.*). The pure nitrile (XI; X = CN) was prepared by heating the chloromethyl compound (38 g.) with cuprous cyanide (38 g.) in phenylacetonitrile (50 c.c.) at 160—170° for 1 hour and then at 220° for ¼ hour. The reaction mixture was decomposed by warming on the water-bath with concentrated hydrochloric acid. After removal of the phenylacetonitrile at reduced pressure, the *nitrile* distilled at 160—170°/0·5 mm. and crystallised from methyl alcohol in colourless prisms, m. p. 66·5—67·5° (Found: C, 86·1; H, 7·0. $C_{14}H_{13}N$ requires C, 86·1; H, 6·7%). Yield, 27·3 g. (75%).

Sodium 3 : 4-dimethyl-1-naphthylacetate (32·5 g.), prepared by the addition of sodium hydroxide (5·6 g.) in water (5 c.c.) to a solution of the acid (30 g.) in alcohol (500 c.c.), was heated with *o*-nitrobenzaldehyde (20·5 g.) and acetic anhydride (180 c.c.) at 130° for 7 hours and then poured into water. After decomposition of the acetic anhydride, the aqueous layer was decanted, and the residue purified through its ammonium salt; the free α-1-(3 : 4-*dimethylnaphthyl*)-o-*nitrocinnamic acid* crystallised from alcohol in yellow tablets (17·5 g.), m. p. 213—214° (Found: C, 72·8; H, 5·2. $C_{21}H_{17}O_4N$ requires C, 72·6; H, 4·9%). The nitro-acid (17·5 g.) was reduced with ferrous sulphate (175 g.) and aqueous ammonia (90 c.c.; *d* 0·880) and water (900 c.c.). The *amino-acid* (XII), purified through its sparingly soluble potassium salt and crystallised from benzene containing a little alcohol, formed a yellow powder (11·5 g.), m. p. 226—227° (Found: C, 79·0; H, 6·1. $C_{21}H_{19}O_2N$ requires C, 79·4; H, 6·05%).

1 : 2-*Dimethylchrysene*-7-*carboxylic acid*. The amino-acid (11·5 g.) was dissolved in water (200 c.c.) containing sodium carbonate (crystalline; 10·5 g.) and sodium nitrite (2·5 g.), and the cold solution slowly run into a solution of sulphuric acid (40·5 c.c.) in water (160 c.c.) cooled in ice. Copper powder was then added and, when the evolution of nitrogen had subsided, the whole was slowly warmed to 70° to complete the reaction. The precipitate was filtered off and extracted with dilute sodium carbonate solution to remove the copper, and the free *acid* reprecipitated from aqueous ammonia (charcoal) and recrystallised from acetic acid; m. p. 234—235° (Found: C, 83·3; H, 5·4. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%). Yield, 3·4 g. Decarboxylation of the acid (3·4 g.) by means of copper powder (1·7 g.) in boiling quinoline (35 c.c.) was complete in 1 hour. The product, distilled over sodium at 200°/0·5 mm., gave 1 : 2-*dimethylchrysene* (VII), m. p. 127—128°, on crystallisation from acetic acid (Found: C, 93·4; H, 6·3. $C_{20}H_{16}$ requires C, 93·7; H, 6·3%). The product obtained by oxidation with sodium dichromate in acetic acid, after removal of acidic material, was a red quinone-like substance, m. p. 157—159°, but it was not possible to obtain it pure enough for analysis.

(ii) 1 : 2-*Dihydroxy*-1 : 2-*dimethyl*-1 : 2-*dihydrochrysene*. To a Grignard solution prepared from methyl iodide (42·6 g.), magnesium (7·2 g.), and ether (200 c.c.) was added finely powdered chrysaquinone (19·3 g.), the whole being cooled in ice. The mixture was then removed from the ice, boiled for ½ hour, and decomposed with ice and ammonium chloride. After removal of the ether the residue was dissolved in methyl alcohol, and the hot solution shaken with a saturated solution of sodium bisulphite until the colour was removed; water was then added, and the *diol* collected and recrystallised from 80% alcohol; it formed colourless needles (14·2 g.), m. p. 154—155° (Found: C, 82·6; H, 6·3. $C_{20}H_{18}O_2$ requires C, 82·7; H, 6·3%).

1 : 2-*Dimethylchrysene*-1 : 2-*oxide* (XIII). Attempts were made to reduce the diol to the hydrocarbon in the same manner as the analogous diaryl diols were reduced by Cook (J., 1931, 2012). The diol (1 g.), hydriodic acid (1 c.c.), and acetic acid (25 c.c.) were refluxed for 10 minutes; after cooling, filtration, and washing, the bimolecular *product* was crystallised from benzene; it had m. p. 245—248°, raised to 258—260° by further crystallisation (Found: C, 92·7; H, 6·2; *M*, 540. $C_{20}H_{16}$ requires C, 93·7; H, 6·3%; *M*, 256). The same product was obtained when the diol (1·5 g.) was heated with hydriodic acid (10 c.c.) and red phosphorus (0·8 g.) in a sealed tube at 175—180° for 18 hours. The diol was recovered unchanged after the passage of hydrogen chloride through its chloroform solution, treatment which converts the diaryl diols obtained from acenaphthenequinone into the dichloro-compounds (Bachmann and Ju Hira-Chu, *J. Amer. Chem. Soc.*, 1936, **58**, 1119). Dehydration to the oxide also presented difficulties; for example, the diol in acetic acid was resinified by strong acids or iodine.

The following method was finally used for the preparation of the oxide: The diol (24 g.) was dissolved in methyl alcohol (350 c.c.), cooled in ice, and hydrogen chloride passed in until the solution was saturated. During this process the oxide commenced to separate; after 4 hours the solid was filtered off, washed with methyl alcohol and water, and dried. The crude oxide (20·5 g.; 91%) had m. p. 153—154° and was sufficiently pure for subsequent experiments. The pure *oxide* separated from benzene–light petroleum in colourless micro-needles, m. p. 155—156° (Found: C, 88·3; H, 6·5. $C_{20}H_{16}O$ requires C, 88·2; H, 5·9%).

(*a*) When a solution of the oxide (1 g.) in acetic acid (30 c.c.) was treated in the cold with hydriodic acid (2 c.c.) in acetic acid (10 c.c.), a precipitate was slowly formed which became resinous on heating. The precipitate, however, if filtered off in the cold could be crystallised from warm acetic acid; the pale yellow needles, m. p. 115°, were very unstable and easily liberated iodine. The crude iodo-compound from 1·2 g. of oxide was suspended in alcohol, zinc dust (3 g.) added, and the whole refluxed for 10 minutes. The zinc was filtered off, the alcohol evaporated to dryness, and the residue extracted with ether. The ethereal solution was washed with water and evaporated, and the residual solid sublimed at 140° in a high vacuum. The sublimate, recrystallised from acetic acid, had m. p. 127—128°, not depressed by 1 : 2-dimethylchrysene prepared as previously described. Yield, 0·4 g.

(*b*) The oxide (5 g.) was dissolved in hot acetic acid (100 c.c.) and shaken in an atmosphere of hydrogen with a platinum catalyst until 375 c.c. were taken up, the temperature being kept at about 60—70°. The filtered solution was evaporated to dryness, and the residue distilled at 250°/1 mm. The distillate, recrystallised from acetic acid, was 1 : 2-dimethylchrysene, m. p. 125—126°; yield, 1·7 g.

(*c*) The oxide (10 g.) was dissolved in acetone (250 c.c.) and shaken at room temperature with palladium in an atmosphere of hydrogen for 18 hours, during which 1950 c.c. were taken up. The filtered acetone solution was evaporated, and the residue distilled, b. p. 194—196°/0·4 mm. (8·5 g.). 1 : 2-*Dihydro*-1 : 2-*dimethylchrysene* crystallised from alcohol in colourless tablets, m. p. 104—104·5° (Found: C, 93·0; H, 7·2. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%). This dihydro-compound (18·5 g.) was smoothly dehydrogenated by platinum at 280—300° to 1 : 2-dimethylchrysene (14 g.), m. p. 126—127°.

Attempted Synthesis of 1 : 2 : 3 : 4-*Tetramethylphenanthrene*.—4-*Keto*-1 : 2 : 3-*trimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (XV). 2-Propionylnaphthalene (Barbot, *Bull. Soc. chim.*, 1930, **47**, 1314) (16 g.) was dissolved in chloroform (80 c.c.), and bromine (4·4 c.c.) in chloroform (40 c.c.) slowly run in. The hydrogen bromide was removed in a current of dry air, and the solvent under reduced pressure. The residual 2-α-*bromopropionylnaphthalene* crystallised from light petroleum in colourless plates, m. p. 81—82° (Found: C, 59·3; H, 4·2. $C_{13}H_{11}OBr$ requires C, 59·3; H, 4·2%). To a solution of ethyl sodiomethylmalonate, prepared from ethyl methylmalonate (60 g.) and sodium (7·5 g.) in benzene (400 c.c.), was added the foregoing bromo-compound (78 g.) in benzene (100 c.c.), the whole being cooled in a freezing mixture. After remaining for 3 hours in the freezing mixture and for 1½ hours at room temperature, it was boiled for 1 hour, the benzene distilled off, and the residue hydrolysed with alcoholic potassium hydroxide. The malonic acid, after separation from the neutral material, was decarboxylated at 190—200°. The acid mixture was esterified with methyl alcohol and hydrogen chloride, and the esters distilled, b. p. 200—210°/4·0 mm. (48 g.). The esters were hydrolysed with alcoholic potassium hydroxide, and the acid, an oily solid, extracted with ether. Crystallisation from benzene and then dilute acetic acid gave β-2-*naphthoyl*-αβ-*dimethylpropionic acid* (XIV), m. p. 147·5—148·5° (Found: C, 74·9; H, 6·3. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%) (45 g. from 180 g. of bromo-compound). The pure *methyl* ester had b. p. 180—187°/1 mm. and crystallised from *cyclo*hexane in colourless plates, m. p. 79·5—80° (Found: C, 75·2; H, 6·7. $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·4%). To a Grignard solution, prepared from methyl iodide (4·5 g.), magnesium (0·4 g.), and ether (15 c.c.), was rapidly added the foregoing ester (2·7 g.) in benzene (120 c.c.) with ice-cooling (compare Haworth and Sheldrick, J., 1934, 864). After heating on the water-bath for 2 hours the mixture was worked up in the usual manner. The crude product obtained from 26 g. of ester was hydrolysed with alcoholic potassium hydroxide, and, after removal of the alcohol and dilution with water, the neutral material removed by ether-extraction. The alkaline solution was then acidified, and the precipitate boiled with sodium carbonate solution; a small amount of the original acid then passed into solution. The major part was undissolved and was collected and distilled, b. p. 180—185°/0·4 mm., and recrystallised from methyl alcohol; it formed colourless plates (16·6 g.) of γ-2-*naphthyl*-αβγ-*trimethylbutyrolactone*, m. p. 131—131·5° (Found: C, 80·15; H, 7·1. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%). The lactone (13 g.), amalgamated zinc (26 g.), water (20 c.c.), concentrated hydrochloric acid (50 c.c.), and toluene (20 c.c.) were boiled under reflux for 48 hours with the addition of hydrochloric acid (10 c.c.) each hour during the first 8 hours. After removal of the toluene with steam the acid–lactone mixture was filtered off and extracted with sodium carbonate solution, 4·2 g. of lactone being recovered. The γ-*naphthyl*-αβγ-*trimethylbutyric acid* went into solution; after purification through its sparingly soluble sodium salt and recrystallisation from light petroleum and then from aqueous methyl alcohol, it had m. p. 124·5—125·5° (Found: C, 79·9; H, 7·9. $C_{17}H_{20}O_2$ requires C, 79·6; H, 7·9%).

Yield, 7·5 g. Ring closure of the acid (6·7 g.) with sulphuric acid (28 c.c.) and water (7 c.c.) was carried out on the water-bath for ½ hour. After dilution with water, the 4-*keto*-1 : 2 : 3-*trimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (XV) was extracted in ether, washed with dilute sodium carbonate solution, recovered, and distilled, b. p. 190°/0·8 mm. (Found: C, 85·9; H, 7·8. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%)

1 : 2 : 3 : 4-*Tetramethylnaphthalene*.—2 : 3-Dimethylnaphthalene (125 g.) was added to a solution of paraformaldehyde (64 g.) in acetic acid (800 c.c.) through which hydrogen chloride had been passed to give a clear solution. The suspension was shaken at room temperature for 24 hours, and the clear solution was worked up as before. The product was distilled, b. p. 142—145°/0·8 mm., and the distillate crystallised from light petroleum. 1-*Chloromethyl*-2 : 3-*dimethylnaphthalene* formed small colourless needles (110 g.), m. p. 86—87° (Found: C, 76·2; H, 6·4. $C_{13}H_{13}Cl$ requires C, 76·2; H, 6·4%). This was reduced quantitatively to 1 : 2 : 3-trimethylnaphthalene, m. p. 27—28°, by shaking an acetone solution in an atmosphere of hydrogen with a palladium catalyst; it gave a picrate, m. p. 142—142·5°, and a styphnate, m. p. 143—144° (Ruzicka and Ehmann, *loc. cit.*, describe the hydrocarbon as an oil and give the m. p. of the picrate 142·5° and of the styphnate 143·5°).

Chloromethylation of 1 : 2 : 3-trimethylnaphthalene (30 g.) with paraformaldehyde (14 g.) in acetic acid (175 c.c.) was carried out as above. After 18 hours' shaking, during which the solid chloromethyl compound separated, it was worked up as before. After distillation at 167°/1·5 mm. 1-*chloromethyl*-2 : 3 : 4-*trimethylnaphthalene* (27·5 g.) separated from light petroleum in colourless tablets, m. p. 94—95° (Found: C, 76·9; H, 6·9. $C_{14}H_{15}Cl$ requires C, 76·85; H, 6·9%). Hydrogenation in acetone solution with a palladium catalyst gave a quantitative yield of 1 : 2 : 3 : 4-*tetramethylnaphthalene*, which separated from alcohol in long colourless needles, m. p. 106·5—107·5° (Found: C, 91·0; H, 8·7. $C_{14}H_{16}$ requires C, 91·3; H, 8·7%). The *picrate* separated from alcohol in vermilion needles, m. p. 182—183° (Found: C, 58·7; H, 4·75. $C_{14}H_{16},C_6H_3O_7N_3$ requires C, 58·1; H, 4·6%).

Oxidation of 1 : 2 : 3 : 4-*Tetramethylnaphthalene*.—The hydrocarbon (1·2 g.) was heated with nitric acid (*d* 1·42; 10 c.c.) and water (20 c.c.) at 175—180° for 7 hours. The solution was evaporated to dryness, and the acids converted into the silver salts in the usual manner. A suspension of the silver salts (2·7 g.) in benzene was treated with methyl iodide (2 c.c.); after 24 hours the solution was filtered and evaporated, and the oily residue dissolved in a little methyl alcohol. On standing for several days at 0°, long needles were deposited, m. p. 179—182°, after recrystallisation from aqueous methyl alcohol. The product did not contain nitrogen. The m. p. in the literature for hexamethyl mellitate is 187—188°. The esters of other acids which might arise in the oxidation of a 1 : 2 : 3 : *x*-tetramethylnaphthalene all melt below 150°.

β-6-(1 : 2 : 3 : 4-*Tetramethylnaphthoyl*)*propionic Acid* (XVI).—A mixture of 1 : 2 : 3 : 4-tetramethylnaphthalene (36·8 g.) and succinic anhydride (24 g.) was added to a solution of aluminium chloride (53·2 g.) in nitrobenzene (160 c.c.) cooled in ice. After 20 hours at 0° the mixture was decomposed with ice and hydrochloric acid, the nitrobenzene distilled off with steam, and the solid dissolved in boiling sodium carbonate solution (charcoal) and filtered. The sodium salt which separated on cooling was filtered off; the *acid* obtained from it crystallised from acetic acid in almost colourless needles (51 g. = 90%), m. p. 196—197° (Found: C, 75·75; H, 7·2. $C_{18}H_{20}O_3$ requires C, 76·0; H, 7·1%).

β-6-(1 : 2 : 3 : 4-*Tetramethylnaphthyl*)*butyric Acid*.—The keto-acid (6·2 g.) was boiled for 6 hours with amalgamated zinc (20 g.), anisole (25 c.c.), water (25 c.c.), and concentrated hydrochloric acid (15 c.c.), more hydrochloric acid (3 c.c.) being added at the end of each hour. The anisole was distilled off with steam, and the residue extracted with dilute sodium carbonate solution. The reprecipitated *acid* crystallised from 80% acetic acid in colourless plates, m. p. 153·5—154·5° (Found: C, 79·7; H, 8·3. $C_{18}H_{22}O_2$ requires C, 79·85; H, 8·2%).

5-*Keto*-1 : 2 : 3 : 4-*tetramethyl*-5 : 6 : 7 : 8-*tetrahydroanthracene*.—The above acid (3·7 g.) was heated with sulphuric acid (12 c.c.) and water (4 c.c.) on a steam-bath for ½ hour, and the deep red solution poured on ice. The solid was washed with dilute sodium carbonate solution and recrystallised from acetic acid (charcoal). The *ketone* separated in pale yellow plates (2·4 g.), m. p. 178—179° (Found: C, 85·45; H, 8·2. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%). The *semicarbazone*, prepared in alcoholic solution, could be recrystallised from dioxan, and had m. p. above 270° (Found: N, 13·2. $C_{19}H_{23}ON_3$ requires N, 13·6%).

1 : 2 : 3 : 4-*Tetramethylanthracene* (XVII).—The aforesaid semicarbazone (16 g.) was heated with sodium ethoxide, prepared from sodium (16 g.) and alcohol (200 c.c.), in eight sealed tubes at 180° for 6 hours. The product was distilled, b. p. 180—185°/0·5 mm. (9·4 g.). 1 : 2 : 3 : 4-*Tetramethyl*-5 : 6 : 7 : 8-*tetrahydroanthracene* separated from alcohol in colourless needles, with a

violet fluorescence, m. p. 127·5—128° (Found : C, 90·5; H, 9·3. $C_{18}H_{22}$ requires C, 90·7; H, 9·3%). The tetrahydro-compound (3·7 g.) was heated with platinum at 320—330° for 6 hours, the product distilled at 200—220°/0·4 mm., and the distillate crystallised from acetic acid. The crystals (2·3 g.) were converted into the *picrate*, which separated from acetic acid in almost black-chocolate needles, m. p. 165—166° (Found : C, 62·6; H, 5·2. $C_{18}H_{18},C_6H_3O_7N_3$ requires C, 62·2; H, 4·6%). Pure 1 : 2 : 3 : 4-*tetramethylanthracene*, regenerated from the picrate and sublimed at 100° in the vacuum of a mercury pump, separated from acetic acid in yellow needles, m. p. 135·5—136·5° (Found : C, 92·4; H, 7·8. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). The hydrocarbon (0·2 g.) and maleic anhydride (0·2 g.) were boiled in xylene (10 c.c.) for 2 hours, and the xylene removed with steam. The residue was boiled with concentrated potassium hydroxide solution, which was then diluted with water and filtered. The filtrate was acidified, and the acid collected and dried (0·25 g.). When crystallised from xylene, it underwent dehydration to the *anhydride*, which separated in fine colourless plates of no definite m. p. and slowly decomposed when heated to 270—290° (Found : C, 79·4; H, 6·25. $C_{22}H_{20}O_3$ requires C, 79·5; H, 6·1%). The adduct was sublimed at 300°/5 mm., and the oily sublimate extracted with boiling potassium hydroxide solution. The insoluble part was recrystallised from acetic acid and had m. p. 130—131°, not depressed by the tetramethylanthracene.

1 : 2 : 3 : 4-*Tetramethylanthraquinone*.—The hydrocarbon (0·5 g.) was boiled in acetic acid (15 c.c.) with sodium dichromate (1 g.) for ½ hour. On cooling, the *quinone* separated in yellow needles, m. p. 232—233° after recrystallisation from acetic acid (Found : C, 81·4; H, 6·2. $C_{18}H_{16}O_2$ requires C, 81·75; H, 6·1%). The quinone gave a deep red vat when its solution in dioxan was boiled with zinc dust and sodium hydroxide solution, but no vat was obtained in the absence of a solvent. The quinone was recovered unchanged after boiling with *o*-phenylenediamine in acetic acid solution, and both behaviours indicate that the compound must be a *p*-quinone.

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