The Preparation of Polycyclic Aromatic Hydrocarbons from Arylpropiolic Acids.

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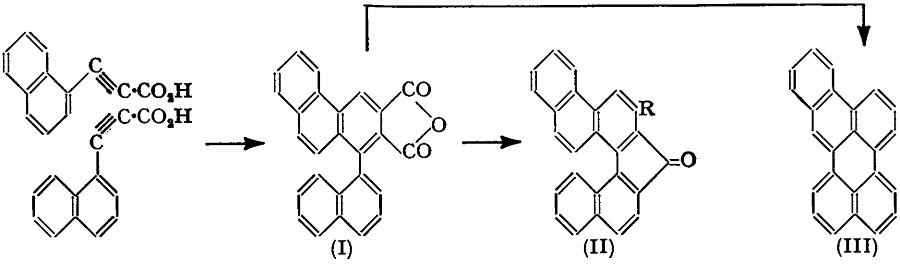
2 : 3-Benzoperylene (III), naphtho(2′ : 3′-1 : 2)pyrene (VI), 1 : 2-3 : 4-5 : 5*a* : 6-11 : 11*a* : 12-tetrabenzonaphthacene (X), and 1 : 2-benzopyrene (XIII) have been synthesised by decarboxylation and cyclodehydrogenation of the products of dimerisation of a series of β-arylpropiolic acids. Several fluorenones have been prepared by decarboxylation of the acids obtained by intramolecular cyclisation of the dimerisation products.

The dimerisation of β-phenylpropiolic acid with acetic anhydride was first reported by Michael and Bucher (*Annalen*, 1895, **28**, 2511) who later (*Amer. Chem. J.*, 1898, **20**, 89) proved the product to be 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride. In later papers Bucher (*J. Amer. Chem. Soc.*, 1908, **30**, 1244; 1910, **32**, 212), Haworth and Sheldrick (*J.*, 1935, 636), Haworth and Kelly (*J.*, 1936, 745), and Baddar and his co-workers (*J.*, 1947, 224; 1948, 1267; 1951, 1844) extended the reaction to substituted phenylpropiolic acids where the structures of many of the products have been proved by alternative syntheses and by degradation. The dimerisation of β-1-naphthylpropiolic acid to give 1-1′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride (I), reported by West (*J. Amer. Chem. Soc.*, 1920, **42**, 1656) and Wojack, Glupe, and Jatzkewitz (*Ber.*, 1938, **71**, 1372), is the only example of this reaction with a polycyclic β-arylpropiolic acid.

In the present work β-arylpropiolic acids (aryl = Ph, 1- and 2-naphthyl, and 9-phenanthryl) were prepared by bromination, followed by dehydrobromination, of the corresponding acrylic acids (Willstaedt and Scheiber, *Ber.*, 1934, **67**, 466; Wojack *et al.*, *loc. cit.*; Reimer, *J. Amer. Chem. Soc.*, 1942, **64**, 2510). Bromination of β-(5 : 6 : 7 : 8-tetrahydro-2-naphthyl)acrylic acid with bromine in carbon tetrachloride or with pyridine hydrobromide perbromide (Rosemund and Kuhnhenn, *Ber.*, 1923, **56**, 1262) took place with the evolution of hydrogen bromide to give, in the latter case, a crystalline dibromo-acid where replacement of hydrogen had taken place. The required tetrahydronaphthylpropiolic acid was synthesised by carboxylation of the Grignard derivative of 6-ethynyl-1 : 2 : 3 : 4-tetrahydronaphthalene which was prepared from 6-acetyl-1 : 2 : 3 : 4-tetrahydronaphthalene by treatment with phosphorus pentachloride followed by dehydrohalogenation.

Refluxing β-1-naphthylpropiolic acid with acetic anhydride gave the dimer, 1-1′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride (I), m. p. 232°, which is much higher than that previously reported by West (*loc. cit.*; m. p. 207—209°) and Wojack *et al.* (*loc. cit.*; m. p. 206°). The insoluble potassium salt derived therefrom was decarboxylated when heated with soda-lime and copper powder under reduced pressure, to give a mixture of 2 : 3-benzoperylene (III), formed by simultaneous dehydrogenation, and 1-1′-naphthylphenanthrene. These products were not readily separated by chromatography, but were separated by means of their 1 : 3 : 5-trinitrobenzene complexes. The two hydrocarbons were also obtained, but in lower yield, by direct distillation of the dry sodium salt formed from the anhydride. Bachmann and Deno (*J. Amer. Chem. Soc.*, 1949, **71**, 3062) prepared 1-1′-naphthylphenanthrene by the dimerisation of 1-vinylnaphthalene to 1 : 2 : 3 : 4-tetrahydro-1-naphthylphenanthrene, followed by dehydrogenation. The absorption spectrum of 2 : 3-benzoperylene (Fig. 1*C*) shows similarities to those of perylene (Clar, *Spectrochim. Acta*, 1950, **4**, 119) and 2 : 3-8 : 9-dibenzoperylene (Clar, *Ber.*, 1932, **65**, 848).

No cyclisation took place on treatment of 1-1′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride (I) with anhydrous hydrogen fluoride although the isomeric 4-2′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride (IV) gave a fluorenone under similar conditions (see below). Cyclisation of the anhydride (I) with aluminium chloride in nitrobenzene gave a good yield of the very sparingly soluble 9-oxo-5 : 6-benzonaphtho(1′ : 2′-3 : 4)-fluorene-1-carboxylic acid (II; R = CO_2H) which was readily decarboxylated to the brick-red 5 : 6-benzonaphtho(1′ : 2′-3 : 4)fluorenone (II; R = H). The carbonyl ring of the latter compound was opened by fusion with potassium hydroxide to give a carboxylic acid which was decarboxylated to 1-1′-naphthylphenanthrene.



Dimerisation of β-2-naphthylpropiolic acid with acetic anhydride gave excellent yields of 4-2′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride (IV). Chromatographic separation of the products obtained by direct decarboxylation of this anhydride by sublimation from copper bronze and soda-lime under reduced pressure gave 4-2′-naphthylphenanthrene together with two isomeric ketones which are probably 7 : 8- (V; R = H) and 6 : 7-benzonaphtho(2′ : 1′-3 : 4)fluorenone (VII). Both these fluorenones gave potassium salts when fused with potassium hydroxide, and the acids obtained from them were decarboxylated to 4-2′-naphthylphenanthrene, showing that the ketones differ only in the point of attachment of the carbonyl group in the naphthalene nucleus. Further, both potassium salts were sublimed from copper bronze to give naphtho(2′ : 3′-1 : 2)pyrene (VI). Intramolecular cyclisation of 4-2′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride with aluminium chloride in nitrobenzene or with anhydrous hydrogen fluoride gave the same keto-acid; on the assumption that normal cyclisation has taken place, with the new ring attached to the α- rather than to the β-position of the naphthalene nucleus, this compound has been given the structure of 9-oxo-7 : 8-benzonaphtho(2′ : 1′-3 : 4)fluorene-1-carboxylic acid (V; R = CO_2H). Decarboxylation with copper bronze in quinoline then gave the red 7 : 8-benzonaphtho(2′ : 1′-3 : 4)fluorenone (V; R = H), m. p. 239°. The two isomeric fluorenones were readily reduced by hydrazine hydrate (Cook and Preston, *J.*, 1944, 553) in good yield to 7 : 8-benzonaphtho(2′ : 1′-3 : 4)fluorene, and 6 : 7-benzonaphtho(2′ : 1′-3 : 4)fluorene, which had similar ultra-violet absorption spectra (Fig. 3*B* and *C*). Buu-Hoï and Cagniant (*Rev. sci.*, 1942, **80**, 436) claim to have prepared 7 : 8-benzonaphtho(2′ : 1′-3 : 4)fluorene by cyclisation of 1 : 2 : 3 : 4-tetrahydro-3-1′-naphthylmethylene-4-oxophenanthrene, but the m. p. (285°) of their product does not correspond with that of either of the hydrocarbons now obtained, and they gave no proof of their formula. Reduction of

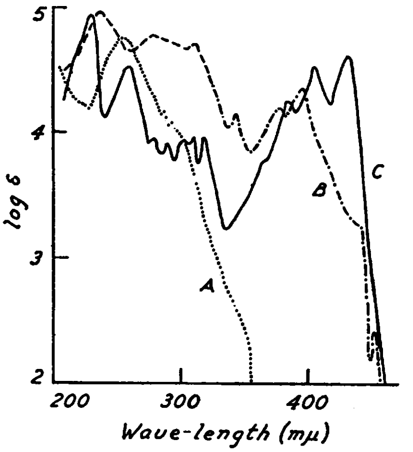


Fig. 1. *Absorption spectra of*: *A*, 1-9′-*phenanthryltriphenylene in* 95% *ethanol*; *B*, 1 : 2-3 : 4-5 : 5*a* : 6-11 : 11*a* : 12-*tetrabenzonaphthacene* (X) — — — — — *in benzene*, — · — · — *in* 95% *ethanol*; *and C*, 2 : 3-*benzoperylene* (III) *in* 95% *ethanol.*

7 : 8-benzonaphtho(2′ : 1′-3 : 4)fluorenone with zinc dust in acetic acid gave the corresponding fluorenol, which on distillation from zinc dust gave 7 : 8-benzonaphtho(2′ : 1′-3 : 4)-fluorene identical with that obtained by reducing the fluorenone with hydrazine hydrate. Cyclodehydrogenation of 4-2′-naphthylphenanthrene with aluminium chloride–sodium chloride at 140° gave only polymerised material, but at temperatures below 120° naphtho-(2′ : 3′-1 : 2)pyrene (VI) was obtained. The absorption spectrum of 4-2′-naphthylphenanthrene (Fig. 2*A*) resembles that of 1-1′-naphthylphenanthrene (Fig. 2*B*) (see also Bachmann and Deno, *J. Amer. Chem. Soc.*, 1949, **71**, 3062) but shows less detail.

FIG 2. *Absorption spectra of*: *A*, *4-2′-naphthylphenanthrene*; *B*, *1-1′-naphthylphenanthrene*; *and C*, *4-phenylphenanthrene*; *all in* 95% *ethanol.*

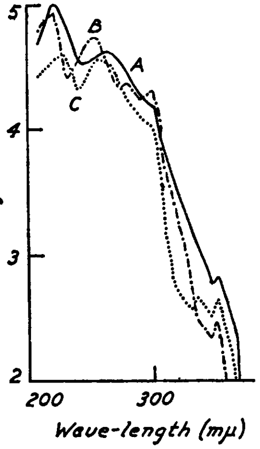
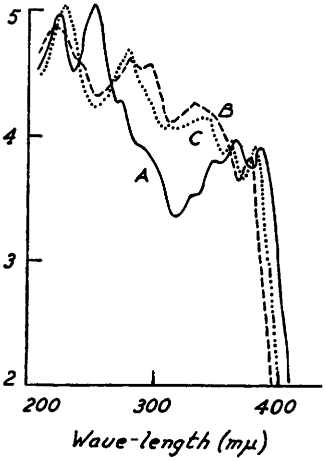
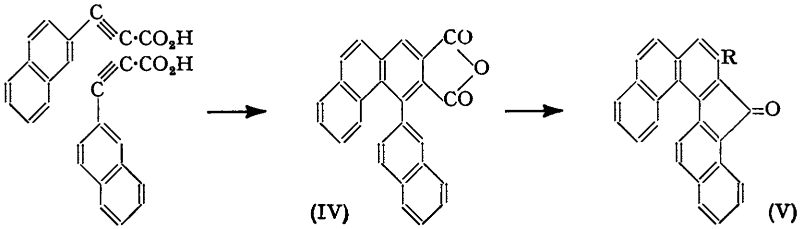


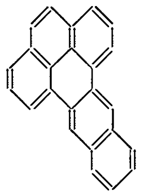
FIG. 3. *Absorption spectra of*: *A*, *1-2′-naphthylanthracene*; *B*, *7 : 8-benzonaphtho*(2′ : 1′-3 : 4)*fluorene*; *and C*, *6 : 7-benzonaphtho*(2′ : 1′-3 : 4)*fluorene*; *all in* 95% *ethanol.*



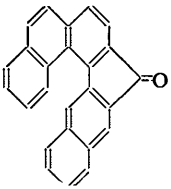
1-9′-Phenanthryltriphenylene-2 : 3-dicarboxylic anhydride (IX), obtained by dimerising β-9-phenanthrylpropiolic acid (VIII), was decarboxylated by heating the dry sodium salt of the acid under reduced pressure with powdered soda-lime and copper powder to give a pale yellow sublimate which was chromatographed on alumina, the products being 1-9′-phenanthryltriphenylene and 1 : 2-3 : 4-5 : 5*a* : 6-11 : 11*a* : 12-tetrabenzonaphthacene (X), the latter being formed by simultaneous decarboxylation and cyclodehydrogenation. 1-9′-Phenanthryltriphenylene, which formed a molecular complex with two molecules of 1 : 3 : 5-trinitrobenzene, gave 1 : 2-3 : 4-5 : 5*a* : 6-11 : 11*a* : 12-tetrabenzonaphthacene on



(IV) (V)

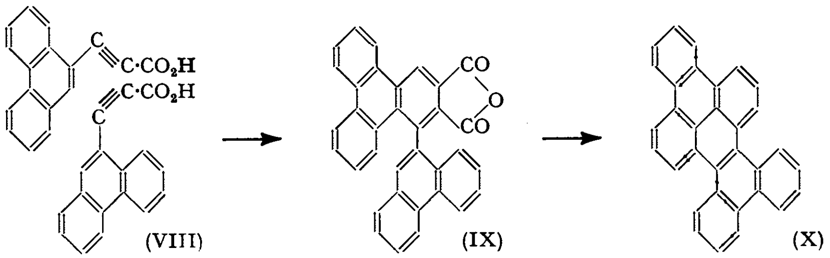


(VI)



(VII)

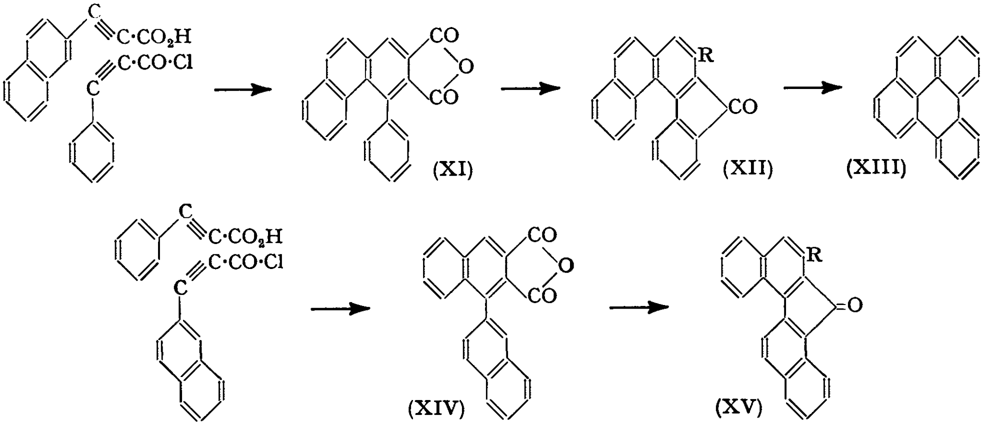
cyclodehydrogenation with palladium–charcoal. The absorption spectrum of 1-9′-phenanthryltriphenylene (Fig. 1*A*) is similar in form to the combined spectra of the two component molecules, but on cyclodehydrogenation the new hydrocarbon (X) gives a spectrum (Fig. 1*B*) showing similarity to that of 1 : 2-6 : 7-dibenzopyrene (Clar, *Ber.*, 1943, **76**, 615).



(VIII) (IX) (X)

In all the above reactions dimerisation was between identical molecules. In order to extend the scope of the reaction to the synthesis of other polycyclic systems the possibility of bringing about a reaction between two dissimilar molecules was investigated. When phenylpropiolic acid and β-2-naphthylpropiolic acid reacted a mixture of three of the four possible combinations was isolated but complete separation proved very tedious: 4-phenylphenanthrene-2 : 3-dicarboxylic anhydride (XI) formed by a " mixed " combination was isolated, together with 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride and 4-2′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride.

Baddar and El-Assal (*J.*, 1951, 1844) treated *o*-methoxyphenylpropiolyl chloride with phenylpropiolic acid, to obtain 1-*o*-methoxyphenyl- and 5-methoxy-1-phenyl-naphthalene-2 : 3-dicarboxylic anhydride, both of which are formed by a " mixed " reaction, and concluded that reaction was preceded by anhydride formation. We found β-phenylpropiolyl chloride and β-2-naphthylpropiolic acid in benzene to give 4-phenylphenanthrene- (XI) and 1-2′-naphthylnaphthalene-2 : 3-dicarboxylic anhydride (XIV). The latter, which was isolated in very small quantity, was characterised by decarboxylation to 1 : 2′-dinaphthyl. Further, on cyclisation with anhydrous aluminium chloride in nitrobenzene the anhydride gave 9-oxo-3 : 4-7 : 8-dibenzofluorene-1-carboxylic acid (XV; R = CO_2H), which was



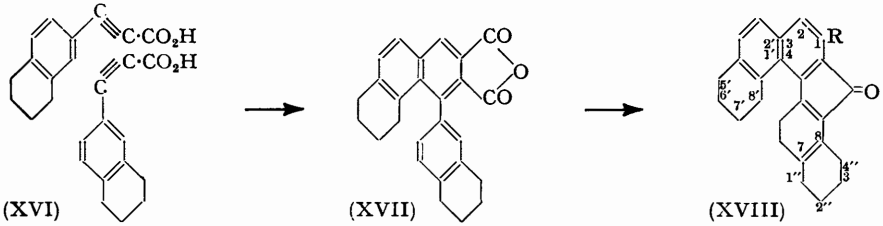
(XI) (XII) (XIII) (XIV) (XV)

decarboxylated with copper bronze in quinoline to 1 : 2-5 : 6-dibenzofluorenone (XV; R = H) previously prepared by Badger (*J.*, 1941, 535) and by Swain and Todd (*J.*, 1941, 674).

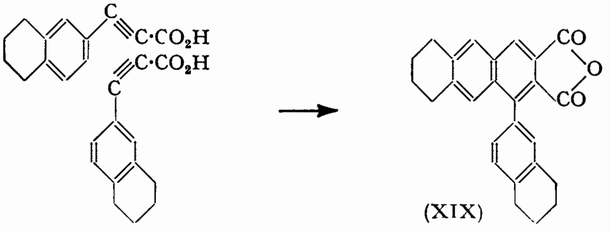
Decarboxylation of 4-phenylphenanthrene-2 : 3-dicarboxylic anhydride by subliming the derived potassium salt from soda-lime and copper powder gave a low yield of 4-phenylphenanthrene and also 1 : 2-benzopyrene (XIII) formed by simultaneous cyclodehydrogenation. The 4-phenylphenanthrene isolated in this reaction failed to give derivatives with picric acid and 1 : 3 : 5-trinitrobenzene, but it had properties identical with a sample prepared by dehydration and dehydrogenation of the product obtained by treating phenyllithium with 1 : 2 : 3 : 4-tetrahydro-4-oxophenanthrene. It is interesting that although phenylmagnesium bromide and 1 : 2 : 3 : 4-tetrahydro-1-oxophenanthrene readily give 1 : 2 : 3 : 4-tetrahydro-1-hydroxy-1-phenylphenanthrene (Bachmann and Wilds, *J. Amer. Chem. Soc.*, 1938, **60**, 624), in a similar reaction with 1 : 2 : 3 : 4-tetrahydro-4-oxophenanthrene only the reduction product, 1 : 2 : 3 : 4-tetrahydro-4-hydroxyphenanthrene, was isolated (Cook, Hewett, and Hieger, *J.*, 1933, 398).

The absorption spectrum of 4-phenylphenanthrene (Fig. 2*C*) shows predominantly the phenanthrene structure and resembles closely that of 4-2′-naphthylphenanthrene. Cyclisation of 4-phenylphenanthrene-2 : 3-dicarboxylic anhydride gave 9-oxonaphtho(2′ : 1′-3 : 4)fluorene-1-carboxylic acid (XII; R = CO_2H) which was decarboxylated to naphtho-(2′-1′-3 : 4)fluorenone (XII; R = H).

Dimerisation of β-(5 : 6 : 7 : 8-tetrahydro-2-naphthyl)propiolic acid (XVI) with acetic anhydride gave a mixture of two isomeric anhydrides which were difficult to separate. Fractional crystallisation gave 5 : 6 : 7 : 8-tetrahydro-4-(5 : 6 : 7 : 8-tetrahydro-2-naphthyl)-phenanthrene-2 : 3-dicarboxylic anhydride (XVII), which was present in the greater quantity. It was characterised by dehydrogenation with palladium–charcoal to 4-2′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride identical with the anhydride prepared by the dimerisation of β-2-naphthylpropiolic acid; and dehydrogenation and decarboxylation of the derived sodium salt of the anhydride (XVII) gave naphtho(2′ : 3′-1 : 2)pyrene. Also cyclisation of the anhydride gave the acid (XVIII; R = CO_2H), which was decarboxylated and dehydrogenated to give the red 7 : 8-benzonaphtho(2′ : 1′-3 : 4)fluorenone (V; R = H) identical with that previously obtained. The combined mother-liquors from the recrystallisation of the anhydride (XVII) yielded more of this anhydride and also some of the isomer (XIX). The sodium salt from this anhydride was dehydrogenated and decarboxylated with copper powder and palladium–charcoal to 1-2′-naphthylanthracene. The absorption spectrum of 1-2′-naphthylanthracene (Fig. 3*A*) shows absorption bands for both anthracene and naphthalene and resembles that of 9 : 10-di-1′-naphthylanthracene (Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 1658).



(XVI) (XVII) (XVIII)



(XIX)

Experimental

1-1′-*Naphthylphenanthrene*-2 : 3-*dicarboxylic Anhydride* (I).—After being refluxed for 2 hr., a solution of β-1-naphthylpropiolic acid (5 g.) in acetic anhydride (20 c.c.) was concentrated to half its volume, and glacial acetic acid (10 c.c.) was added. After cooling, the anhydride (3·8 g.) separated as fine needles, m. p. 232° (from glacial acetic acid) (Found : C, 83·6; H, 3·9. Calc.

for $C_{26}H_{14}O_3$: C, 83·4; H, 3·7%). West (*loc. cit.*) gives m. p. 207—209°. Wojack *et al.* (*loc. cit.*) give m. p. 206°.

2 : 3-*Benzoperylene* (III).—1-1′-Naphthylphenanthrene-2 : 3-dicarboxylic anhydride (4·5 g.) was dissolved in methyl-alcoholic potassium hydroxide (6 c.c. of a 25% solution) and the solution was evaporated to dryness on a water-bath. An intimate mixture of this potassium salt, powdered soda-lime (10 g.), and copper powder (4 g.) was heated in a test-tube, gradually at first, inside a Pyrex glass tube at 0·2 mm. in the presence of a slow stream of carbon dioxide. Even distribution of heat was obtained by using a T burner and a copper tube to surround the heated portion of the Pyrex tube. When no further sublimate condensed on the walls of the Pyrex tube, heating was stopped and the semi-solid sublimate was taken up in hot benzene–ethanol and treated with 1 : 3 : 5-trinitrobenzene (4·0 g.) in ethanol. Fine red-brown needles of the *trinitrobenzene* complex of 2 : 3-benzoperylene (0·6 g.) separated on cooling; this had m. p. 208—209° (from ethanol) (Found: C, 70·1; H, 3·5. $C_{30}H_{17}O_6N_3$ requires C, 69·9; H, 3·3%). The filtrate after concentration and treatment with charcoal deposited yellow crystals (2·2 g.) of the *trinitrobenzene* complex of 1-1′-naphthylphenanthrene, m. p. 152—153° (from ethanol) (Found: N, 8·3. $C_{30}H_{19}O_6N_3$ requires N, 8·1%). The latter complex (1·8 g.) was decomposed by stannous chloride (8·0 g.) in boiling 50% aqueous ethanol (40 c.c.) containing concentrated hydrochloric acid (30 c.c.), to give a white precipitate of 1-1′-naphthylphenanthrene (0·8 g.), m. p. 115° (from ethanol). It gave an orange picrate, m. p. 135°. Bachmann and Deno (*loc. cit.*) give m. p. 115—116° and picrate, m. p. 135—136°. The trinitrobenzene complex of 2 : 3-benzoperylene was similarly decomposed and gave 2 : 3-*benzoperylene* as deep yellow plates, m. p. 200—201° (from benzene or ethanol) after chromatography in benzene on alumina (Found: C, 95·6; H, 4·7. $C_{24}H_{14}$ requires C, 95·4; H, 4·6%). It gave a blue fluorescence in ethanol.

1-1′-Naphthylphenanthrene (0·2 g.) was refluxed for 1 hr. with copper bronze (0·2 g.). The resulting oil was taken up in hot benzene–ethanol and after addition of 1 : 3 : 5-trinitrobenzene a small quantity of the red-brown complex with 2 : 3-benzoperylene separated, on cooling, as needles, m. p. 207°.

9-*Oxo*-5 : 6-*benzonaphtho*(1′ : 2′-3 : 4)*fluorene*-1-*carboxylic Acid* (II; R = CO_2H).—1-1′-Naphthylphenanthrene-2 : 3-dicarboxylic anhydride (2·5 g.) was dissolved in nitrobenzene (30 c.c.) and cooled to 0°; anhydrous aluminium chloride (4 g.) was then added during 10 min. with cooling. After 4 hr. at room temperature and 10 min. at 50° the mixture was poured on ice and hydrochloric acid. The residue remaining after steam-distillation was broken up, filtered off, and recrystallised from a large volume of xylene–acetic acid, to give the *acid* as brown-grey needles (2·1 g.), m. p. 333—335° (Found: C, 83·1; H, 4·0. $C_{26}H_{14}O_3$ requires C, 83·4; H, 3·7%).

5 : 6-*Benzonaphtho*(1′-2′-3 : 4)*fluorenone* (II; R = H).—The foregoing acid (1·3 g.) was heated on an oil-bath at 200—210° for 2 hr. with copper powder (1 g.) in quinoline (15 c.c.). The cooled, filtered solution was poured into dilute hydrochloric acid, and the precipitate was filtered off and taken up in benzene (charcoal). Bright brick-red clusters of fine needles of 5 : 6-*benzonaphtho*(1′ : 2′-3 : 4)*fluorenone* (0·7 g.) which separated on cooling had m. p. 245° (Found: C, 90·6; H, 4·5. $C_{25}H_{14}O$ requires C, 90·9; H, 4·3%). This readily gave an *oxime*, m. p. 260—261°, as clusters of fine orange needles from aqueous ethanol (Found: N, 4·0. $C_{25}H_{15}ON$ requires N, 4·1%). The fluorenone (50 mg.) was heated to 300—310° for 10 min. with potassium hydroxide (0·5 g.), and the cooled melt was dissolved in water and acidified, to give an acid which was decarboxylated to 1-1′-naphthylphenanthrene (identified as the trinitrobenzene complex, m. p. 152°) by copper bronze in boiling quinoline.

αβ-*Dibromo*-β-2-*naphthylpropionic Acid*.—β-2-Naphthylacrylic acid (4·5 g.), suspended in carbon tetrachloride (50 c.c.), was treated during 15 min. with a slight excess of bromine (3·8 g.) in carbon tetrachloride (20 c.c.) in the presence of strong artificial light. Then the suspension was stirred occasionally for 1 hr. and next concentrated almost to dryness in a current of air at room temperature. The precipitate was filtered off and washed with carbon tetrachloride. Recrystallisation from chloroform gave the *dibromo-acid* (6·5 g.) as fine white needles, m. p. 188° (decomp.) (Found: C, 43·7; H, 3·0. $C_{13}H_{10}O_2Br_2$ requires C, 43·6; H, 2·8%).

β-2-*Naphthylpropiolic Acid*.—αβ-Dibromo-β-2-naphthylpropionic acid (34 g.) was dissolved in methanol (50 c.c.), and heated with potassium hydroxide in methanol (100 c.c. of 25% solution) on a steam-bath. After evaporation to dryness the solid residue was taken up in methanol (50 c.c.) and again evaporated to dryness. The residue was then dissolved in water, chilled, and acidified. The precipitated *acid* was recrystallised from carbon tetrachloride as white needles (19·5 g.), m. p. 143—144° with previous softening (Found: C, 79·4; H, 4·3. $C_{13}H_8O_2$ requires C, 79·6; H, 4·1%).

4-2′-Naphthylphenanthrene-2 : 3-dicarboxylic Anhydride (IV).—β-2-Naphthylpropiolic acid (15 g.) was refluxed for 1 hr. with acetic anhydride (60 c.c.); acetic acid (30 c.c.) was then added. The precipitate which formed on cooling was recrystallised from a large volume of acetic acid (charcoal), to give the *anhydride* (11 g.), m. p. 265° (Found : C, 83·0; H, 4·1. $C_{26}H_{14}O_3$ requires C, 83·4; H, 3·7%).

Decarboxylation of 4-2′-Naphthylphenanthrene-2 : 3-dicarboxylic Anhydride (IV).—A mixture of 4-2′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride (10 g.), powdered soda-lime (25 g.), and copper powder (5 g.) was heated at 0·2 mm. in the presence of carbon dioxide until no further sublimate condensed. The sublimate was taken up in benzene, concentrated, and chromatographed on alumina to give three fractions. The first was concentrated to give white needles of *4-2′-naphthylphenanthrene* (3·0 g.), m. p. 105—106° (from ethanol) (Found : C, 94·4; H, 5·6. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%). The second fraction yielded clusters of red needles of 7 : 8-*benzonaphtho*(2′ : 1′-3 : 4)*fluorenone* (V; R = H) (0·45 g.), m. p. 239° from benzene (Found : C, 90·9, 90·7; H, 4·6, 4·3. $C_{25}H_{14}O$ requires C, 90·9; H, 4·2%) [*oxime*, m. p. 230—231°, orange needles from ethanol (Found : N, 4·0. $C_{25}H_{15}ON$ requires N, 4·1%)]. The third fraction, 6 : 7-*benzonaphtho*(2′ : 1′-3 : 4)*fluorenone* (VII) (0·95 g.), m. p. 203—204°, lemon-yellow needles from benzene (Found : C, 91·0; H, 4·6%), gave an *oxime*, m. p. 265°, as yellow needles from ethanol (Found : N, 4·0%), and a 2 : 4-*dinitrophenylhydrazone*, m. p. 321—323°, as red needles from ethanol (Found : N. 10·9. $C_{31}H_{18}O_4N_4$ requires N, 11·0%).

7 : 8-Benzonaphtho(2′ : 1′-3 : 4)fluorenone (0·2 g.) was heated at 280—300° for ½ hr. with potassium hydroxide (1·0 g.). The crude potassium salt which floated on the melt was removed, ground with copper powder (0·2 g.), and sublimed at 0·2 mm./360°, to give naphtho(2′ : 3′-1 : 2)-pyrene (VI), m. p. and mixed m. p. 259—260° (from benzene) [picrate, red-brown needles (from benzene), m. p. 213°]. Clar (*J.*, 1949, 2168) gives hydrocarbon, m. p. 259—260°, and picrate, m. p. 212—213°. 6 : 7-Benzonaphtho(2′ : 1′-3 : 4)fluorenone also gave naphtho(2′ : 3′-1 : 2)-pyrene when similarly treated.

7 : 8-Benzonaphtho(2′ : 1′-3 : 4)fluorenone (0·15 g.) was heated at 280—300° for ½ hr. with potassium hydroxide (1·0 g.), and the cooled melt was dissolved in warm water and acidified with dilute hydrochloric acid. The liberated acid was filtered off, dried, and heated for 2 hr. with copper bronze (0·2 g.) in quinoline (4 c.c.) at 210—220°. The product was worked up as previously described, to give 4-2′-naphthylphenanthrene m. p. 105—106° (from ethanol), after purification by chromatography on alumina. The same hydrocarbon was obtained when 6 : 7-benzonaphtho(2′ : 1′-3 : 4)fluorenone was similarly treated.

7 : 8-*Benzonaphtho*(2′ : 1′-3 : 4)*fluorene*.—7 : 8-Benzonaphtho(2′ : 1′-3 : 4)fluorenone (0·28 g.) was heated at 200—210° for 6 hr. in a sealed tube with 85% hydrazine hydrate (0·6 c.c.). The solid product was taken up in benzene, chromatographed on alumina, and crystallised from ethanol–benzene, to give the *fluorene* (0·21 g.) as flat needles, m. p. 138—139° (Found : C, 95·0; H, 5·2. $C_{25}H_{16}$ requires C, 94·9; H, 5·1%). It gave a *dipicrate*, red-brown needles, m. p. 175—176° (Found : N, 10·8. $C_{37}H_{22}O_{14}N_6$ requires N, 10·9%).

6 : 7-*Benzonaphtho*(2′ : 1′-3 : 4)*fluorene*.—6 : 7-Benzonaphtho(2′ : 1′-3 : 4)fluorenone (0·12 g.) was reduced by hydrazine hydrate (0·3 c.c.) as just described. After chromatography in benzene on alumina the *fluorene* (80 mg.) was obtained as long white needles, m. p. 182—183° (Found : C, 94·5; H, 5·4. $C_{25}H_{16}$ requires C, 94·9; H, 5·1%). It gave a brick-red *dipicrate*, m. p. 176° (Found : N, 10·6%), which depressed the melting point of the previous dipicrate.

9-*Oxo*-7 : 8-*benzonaphtho*(2′ : 1′-3 : 4)*fluorene*-1-*carboxylic Acid* (V; R = CO_2H).—(*a*) 4-2′-Naphthylphenanthrene-2 : 3-dicarboxylic anhydride (30 g.) was set aside for 3 days with anhydrous hydrogen fluoride (approx. 40 c.c.). The brown solid remaining after the hydrogen fluoride had evaporated was insoluble in alkali. It was recrystallised from a large volume of acetic acid (charcoal), to give the *acid* (2·5 g.) as fibrous grey-brown needles, m. p. 295—296° (Found : C, 82·8; H, 4·2. $C_{26}H_{14}O_3$ requires C, 83·4; H, 3·7%).

(*b*) 4-2′-Naphthylphenanthrene-2 : 3-dicarboxylic anhydride (1·8 g.) in nitrobenzene (20 c.c.) was treated with anhydrous aluminium chloride (1·4 g.) at room temperature, warmed at 50—60° for 2 hr., and poured into dilute hydrochloric acid. After removal of the nitrobenzene in steam the residue recrystallised from acetic acid, to give the acid (1·2 g.), m. p. 294—296°.

7 : 8-*Benzonaphtho*(2′ : 1′-3 : 4)*fluorenone* (V; R = H).—The above acid (0·2 g.) was heated for 1½ hr. with copper powder (0·2 g.) in quinoline (3 c.c.). The filtered, cooled solution was poured into dilute hydrochloric acid, and the solid filtered off and recrystallised from benzene (charcoal), to give 7 : 8-benzonaphtho(2′ : 1′-3 : 4) fluorenone (0·11 g.), m. p. 238—239° undepressed on mixing with the previous sample.

9-*Hydroxy*-7 : 8-*benzonaphtho*(2′ : 1′-3 : 4)*fluorene*.—7 : 8-Benzonaphtho(2′ : 1′-3 : 4)fluorenone (0·25 g.) was heated at 100° for 3 hr. with zinc dust (5 g.) in acetic acid (30 c.c.). The solution was filtered and poured into water, and the white solid was filtered off and recrystallised from ethanol (charcoal), to give the *hydroxyfluorene* (0·18 g.) as colourless needles, m. p. 207° (Found : C, 89·8; H, 5·0. $C_{25}H_{16}O$ requires C, 90·3; H, 4·8%). When distilled from zinc dust this gave 7 : 8-benzonaphtho(2′ : 1′-3 : 4)fluorene, m. p. 138—139° after chromatography in benzene on alumina.

Naphtho(2′ : 3′-1 : 2)*pyrene* (VI).—4-2′-Naphthylphenanthrene (0·3 g.) was added at once and stirred into a melt of anhydrous aluminium chloride (2·5 g.) and sodium chloride (0·5 g.) at 120°. The mixture was allowed to cool to 90° during 5 min. Ice and hydrochloric acid were added and the solid was filtered off, taken up in benzene, dried, and chromatographed on alumina, to give naphtho(2′ : 3′-1 : 2)pyrene, m. p. and mixed m. p. 258—259°.

αβ-*Dibromo*-β-9-*phenanthrylpropionic Acid.*—β-9-Phenanthrylacrylic acid (Bachmann and Kloetzel, *J. Amer. Chem. Soc.*, 1937, **59**, 2207) (6·5 g.) was suspended in chloroform (30 c.c.), and bromine (3 g.) in carbon tetrachloride (20 c.c.) was added (10 min.) with stirring in the presence of bright artificial light at room temperature. After 2 hr. the solution was evaporated to approx. 20 c.c. in a current of air, and the *dibromo-acid* was filtered off, washed with carbon tetrachloride, and recrystallised from acetic acid, to give white needles (4·3 g.), m. p. 206—207° (decomp.) (Found : C, 50·5; H, 3·2. $C_{17}H_{12}O_2Br_2$ requires C, 50·1; H, 2·9%).

β-9-*Phenanthrylpropiolic Acid* (VIII).—The above dibromo-acid (4·2 g.), suspended in methanol (20 c.c.), was treated with potassium hydroxide in methanol (30 c.c. of a 20% solution), and the whole was evaporated to dryness on a steam-bath. The evaporation was repeated twice after the addition of further methanol (50 c.c.), and the residue was then taken up in water, chilled, and acidified, to give β-9-*phenanthrylpropiolic acid* (2·4 g.), m. p. 182—183° (Found : C, 82·5; H, 3·6. $C_{17}H_{10}O_2$ requires C, 82·9; H, 4·1%).

1-9′-*Phenanthryltriphenylene*-2 : 3-*dicarboxylic Anhydride* (IX).—β-9-Phenanthrylpropiolic acid (2·2 g.) was refluxed for 2 hr. with acetic anhydride (20 c.c.), concentrated to 10 c.c., and poured into glacial acetic acid (10 c.c.). The crystalline solid which separated on cooling was recrystallised from acetic acid, to give the *anhydride* (1·8 g.) as pale lemon-yellow crystals, m. p. 325—327° (Found : C, 86·3; H, 4·1. $C_{34}H_{18}O_3$ requires C, 86·1; H, 3·8%).

1 : 2-3 : 4-5 : 5a : 6-11 : 11a : 12-*Tetrabenzonaphthacene* (X).—(*a*) 1-9′-Phenanthryltriphenylene-2 : 3-dicarboxylic anhydride (0·8 g.) was taken up in methanol (20 c.c.) containing sodium hydroxide (0·5 g.), and the solution was evaporated to dryness. This sodium salt was mixed with powdered soda-lime (6 g.) and copper powder (5 g.) and heated in the presence of carbon dioxide at 0·3 mm. until decarboxylation and sublimation were complete. The sublimate was chromatographed in benzene on alumina and eluted with benzene. The first fraction, recrystallised from benzene–ethanol, gave colourless clusters of needles of 1-9′-*phenanthryltriphenylene* (0·15 g.), m. p. 216—217° (Found : C, 94·8; H, 5·0. $C_{32}H_{20}$ requires C, 95·0; H, 5·0%). With 2 mols. of 1 : 3 : 5-trinitrobenzene it gave a *derivative*, m. p. 178°, as yellow needles from ethanol (Found : N, 10·3. $C_{44}H_{26}O_{12}N_6$ requires N, 10·1%). 1 : 2-3 : 4-5 : 5a - 6-11 : 11a : 12-*Tetrabenzonaphthacene* (30 mg.) was eluted from the column by a large volume of benzene and recrystallised from xylene as pale yellow needles m. p. 289—290° (Found : C, 95·4; H, 4·5. $C_{32}H_{18}$ requires C, 95·5; H, 4·5%).

(*b*) 1-9′-Phenanthryltriphenylene (70 mg.) was heated at 400° for 3 hr. with 10% palladium–charcoal (40 mg.). The resulting product was chromatographed in benzene on alumina, to give 1 : 2-3 : 4-5 : 5*a* : 6-11 : 11*a* : 12-tetrabenzonaphthacene, m. p. 289—290°, preceded by a small quantity of unchanged starting material.

Interaction of Phenylpropiolic Acid and β-2-*Naphthylpropiolic Acid.*—β-2-Naphthylpropiolic acid (3·0 g.) and β-phenylpropiolic acid (4·5 g.) were each dissolved in acetic acid (25 c.c.) and then mixed. Acetic anhydride (30 c.c.) was added and the resulting solution was refluxed for 2 hr. and concentrated to approx. 20 c.c. The crystalline product precipitated on cooling was recrystallised from a large volume of glacial acetic acid, to give 4-*phenylphenanthrene*-2 : 3-*dicarboxylic anhydride* (XI) (0·6 g.), m. p. 283°, as flat needles (Found : C, 81·4; H, 3·5. $C_{22}H_{12}O_3$ requires C, 81·5; H, 3·7%). The solid which separated on further concentration of the mother liquors was recrystallised, to give 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride (2·4 g.), m. p. 252° (Baddar, *J.*, 1948, 1267, gives m. p. 252—253°) (Found : C, 78·4; H, 3·9. Calc. for $C_{18}H_{10}O_3$: C, 78·8; H, 3·7%), and 4-2′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride (0·4 g.), m. p. 265°.

Reaction of β-*Phenylpropiolyl Chloride with* β-2-*Naphthylpropiolic Acid.*—β-Phenylpropiolyl chloride (4·5 g.) and β-2-naphthylpropiolic acid (6·0 g.) were refluxed for 48 hr. in benzene (60 c.c.). After a further 48 hr., at room temperature. the crystalline precipitate was filtered off and recrystallised from acetic acid, to give 4-phenylphenanthrene-2 : 3-dicarboxylic anhydride (XI) (2·5 g.), m. p. 283°. Concentration of the acetic acid mother-liquors gave 1-2′-*naphthylnaphthalene*-2 : 3-*dicarboxylic anhydride* (XIV) which recrystallised from benzene as needles (0·12 g.), m. p. 218° (Found: C, 81·1; H, 3·9. $C_{22}H_{12}O_3$ requires C, 81·5; H, 3·7%). The anhydride (*ca.* 50 mg.) was heated at 210—220° for 2 hr. with copper bronze (0·1 g.) in quinoline (2 c.c.). The product was worked up in the usual manner, chromatographed in benzene on alumina, and treated with an excess of picric acid in ethanol, to give the picrate of 1 : 2′-dinaphthyl as orange needles, m. p. 123—124°. A solution of the picrate in benzene was passed down a column of alumina to give the hydrocarbon, m. p. 72—73°. Hooker and Fieser (*J. Amer. Chem. Soc.*, 1936, **58**, 1216) give m. p. of 1 : 2′-dinaphthyl as 74·5—75° and of picrate as 127—127·5° (corr.).

1 : 2-*Benzopyrene* (XIII) *and* 4-*Phenylphenanthrene*.—The dry potassium salt prepared from 4-phenylphenanthrene-2 : 3-dicarboxylic anhydride (1·0 g.) was decarboxylated by heat at 0·2 mm. with copper powder (2 g.) and soda-lime (5·0 g.) in nitrogen. The sublimate was taken up in benzene and chromatographed on alumina to give, in the first fraction, 4-phenylphenanthrene (40 mg.), m. p. 80—81° (white crystals from ethanol) undepressed on admixture with a specimen prepared from 1 : 2 : 3 : 4-tetrahydro-4-oxophenanthrene. The second fraction (pale yellow), after concentration, gave 1 : 2-benzopyrene (0·11 g.) very pale yellow plates, m. p. and mixed m. p. 175° (from benzene); this gave red-brown needles of the picrate, m. p. 226°, from ethanol. Cook and Hewett (*J.*, 1933, 395) give hydrocarbon, m. p. 178°, and picrate, m. p. 229—230°; the complex with 1 : 3 : 5-*trinitrobenzene* crystallised from ethanol as orange needles, m. p. 253—254° (Found: N, 9·1. $C_{26}H_{15}O_6N_3$ requires N, 9·0%).

9-*Oxonaphtho*(2′ : 1′-3 : 4)*fluorene*-1-*carboxylic Acid* (XII; R = CO_2H).—4-Phenylphenanthrene-2 : 3-dicarboxylic anhydride (0·15 g.) in nitrobenzene (5 c.c.) was treated with anhydrous aluminium chloride (0·12 g.) and warmed at 50° for 0·5 hr. The dark red solid obtained by working up in the usual manner crystallised from acetic acid, to give 9-*oxonaphtho*(2′ : 1′-3 : 4)-*fluorene*-1-*carboxylic acid* (0·11 g.), m. p. 240° (Found: C, 81·4; H, 3·9. $C_{22}H_{12}O_3$ requires C, 81·5; H, 3·7%).

Naphtho(2′ : 1′-3 : 4)*fluorenone* (XII; R = H).—The above acid (*ca.* 80 mg.) was decarboxylated at 210° for 0·5 hr. with copper bronze (0·1 g.) in quinoline (1 c.c.). This gave *naphtho*(2′ : 1′-3 : 4)*fluorenone* (*ca.* 20 mg.), m. p. 148—149°, orange needles from ethanol (charcoal) (Found: C, 89·5; H, 4·3. $C_{21}H_{12}O$ requires C, 90·0; H, 4·3%).

9-*Oxo*-3 : 4-7 : 8-*dibenzofluorene*-1-*carboxylic Acid* (XV; R = CO_2H).—1-2′-Naphthylnaphthalene-2 : 3-dicarboxylic anhydride (0·1 g.) in nitrobenzene (5 c.c.) was heated with anhydrous aluminium chloride (0·1 g.) at 50° for 2 hr., giving the *acid* (90 mg.), m. p. 260—261° (brown needles from benzene) (Found: C, 81·0; H, 3·7. $C_{22}H_{12}O_3$ requires C, 81·5; H, 3·7%). The acid, with copper bronze in quinoline at 210° (3 hr.), gave, after sublimation of the product from soda-lime, 1 : 2-5 : 6-dibenzofluorenone, m. p. 164°, red cubes (from ethyl acetate). Badger (*J.*, 1941, 535) gives m. p. 164°.

1 : 2 : 3 : 4-*Tetrahydro*-4-*hydroxy*-4-*phenylphenanthrene*.—Bromobenzene (3·0 g.) in dry ether (30 c.c.) was treated with lithium (0·25 g.) with rapid stirring for 1 hr., most of the lithium reacting. 1 : 2 : 3 : 4-Tetrahydro-4-oxophenanthrene (2·5 g.) in ether (10 c.c.) was added dropwise and the mixture stirred for 3 hr. during which a complex settled out. The ether solution was decanted, and the solid was washed with dilute hydrochloric acid, filtered off, and recrystallised from benzene–light petroleum, to give 1 : 2 : 3 : 4-*tetrahydro*-4-*hydroxy*-4-*phenylphenanthrene* (1·6 g.) as large cubes, m. p. 108—109° (Found: C, 87·5; H, 6·4. $C_{20}H_{18}O$ requires C, 87·6; H, 6·6%).

1 : 2-*Dihydro*-4-*phenylphenanthrene*.—The above hydroxy-compound (1·2 g.) was distilled (b. p. 240—245°/20 mm.), to give 1 : 2-*dihydro*-4-*phenylphenanthrene* (1·0 g.) as a thick syrup which slowly crystallised. Recrystallisation from ethanol gave the hydrocarbon as colourless needles, m. p. 99—100° (Found: C, 93·4; H, 6·3. $C_{20}H_{16}$ requires C, 93·7; H, 6·3%).

4-*Phenylphenanthrene*.—The dihydro-compound (0·5 g.) was refluxed at 300—310° for 1 hr. with 5% palladium–charcoal (0·3 g.). Chromatography in benzene on alumina gave 4-*phenylphenanthrene* (0·25 g.) as colourless rods, m. p. 81° (Found: C, 94·1; H, 5·5. $C_{20}H_{14}$ requires C, 94·5; H, 5·5%), together with 1 : 2-benzopyrene isolated as the trinitrobenzene derivative (*ca.* 20 mg.; m. p. 252—253°).

6-1′-*Chlorovinyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—Phosphorus pentachloride (134 g.) and 6-acetyl-1 : 2 : 3 : 4-tetrahydronaphthalene (110 g.) were heated at 70° for 15 min. Fractionation under reduced pressure gave phosphorus oxychloride and then the *chloroethylene* (70 g.), b. p. 130—135°/16 mm. (Found: C, 75·2; H, 6·4. $C_{12}H_{13}Cl$ requires C, 74·8; H, 6·7%).

6-*Ethynyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—The above chloroethylene (69 g.) was refluxed on a water-bath for 5 hr. with potassium hydroxide (50 g.) in ethanol (100 c.c.). The solution was poured into ice-water, and the oil which separated was extracted with ether and distilled, to give the *acetylene* (33 g.), b. p. 110—112°/2 mm. (Found : C, 92·5; H, 7·7. $C_{12}H_{12}$ requires C, 92·3; H, 7·7%).

β-(5 : 6 : 7 : 8-*Tetrahydro*-2-*naphthyl*)*propiolic Acid* (XVI).—6-Ethynyl-1 : 2 : 3 : 4-tetrahydronaphthalene (12 g.) in dry ether (50 c.c.) was added dropwise to a Grignard reagent prepared from magnesium (3 g.), ethyl bromide (14 g.), and ether (50 c.c.). After 3 hours' refluxing the mixture was poured on a large excess of solid carbon dioxide and left for 8 hr. Cold dilute hydrochloric acid was added and the ether layer separated and extracted with dilute sodium hydroxide. Acidification of the cold alkaline extracts gave the acetylenic *acid* (8 g.), m. p. 114—115° (from carbon tetrachloride; slight orange colour) (Found : C, 78·2; H, 6·6. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%).

Dimerisation of β-(5 : 6 : 7 : 8-*Tetrahydro*-2-*naphthyl*)*propiolic Acid*.—The above acid (6·0 g.) was refluxed for 2 hr. with acetic anhydride (30 c.c.) and after the addition of acetic acid (20 c.c.) and water (10 c.c.) the solution was concentrated to about 20 c.c. The solid which separated on cooling was recrystallised several times from glacial acetic acid and benzene–light petroleum, to give 5 : 6 : 7 : 8-*tetrahydro*-4-(5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl*)*phenanthrene*-2 : 3-*dicarboxylic anhydride* (XVII) (1·6 g.) as colourless flat needles, m. p. 204—205° (Found : C, 81·6; H, 6·0. $C_{26}H_{22}O_3$ requires C, 81·7; H, 5·8%). The combined mother-liquors were concentrated, benzene and light petroleum were added, and the solution was set aside for several days to crystallise slowly. Large pale green cubes crystallised among hard clusters of crystals. These were filtered off and separated by hand, and each recrystallised from acetic acid and benzene–light petroleum. 5 : 6 : 7 : 8-*Tetrahydro*-1-(5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl*)*anthracene*-2 : 3-*dicarboxylic anhydride* (XIX) (0·9 g.), m. p. 194—195° depressed on admixture with the previously isolated anhydride, was obtained from the pale green cubes as fine white needles (Found : C, 81·6; H, 5·5. $C_{26}H_{22}O_3$ requires C, 81·7; H, 5·8%). The hard clusters of crystals yielded a further quantity of the anhydride previously isolated (1·2 g.).

The anhydride (XVII) (0·2 g.) was heated at 320—340° for ½ hr. with 30% palladium–charcoal (50 mg.). Recrystallisation from acetic acid (charcoal) gave colourless needles of 4-2′-naphthylphenanthrene-2 : 3-dicarboxylic anhydride (IV), m. p. 264—265°, undepressed on admixture with that prepared by the dimerisation of β-2-naphthylpropiolic acid.

Naphtho(2′ : 3′-1 : 2)*pyrene* (VI).—5 : 6 : 7 : 8-Tetrahydro-4-(5 : 6 : 7 : 8-tetrahydro-2-naphthyl)phenanthrene-2 : 3-dicarboxylic anhydride (0·9 g.) was dissolved in dilute aqueous sodium hydroxide containing a little ethanol, and was concentrated until the sodium salt began to be precipitated. The semi-solid sodium salt which separated on cooling was washed by decantation, dried, and thoroughly mixed with 30% palladium–charcoal (0·1 g.) and copper powder (1·0 g.) After being heated at 320—360° for 4 hr. the mixture was dry-distilled and the condensate was chromatographed in benzene on alumina, to give naphtho(2′ : 3′-1: 2)pyrene (0·18 g.), m. p. and mixed m. p. 258—259°.

5′ : 6′ : 7′ : 8′-1″ : 2″ : 3″ : 4″-*Octahydro*-9-*oxo*-7 : 8-*benzonaphtho*(2′ : 1′-3 : 4)*fluorene*-1-*carboxylic Acid* (XVIII; R = CO_2H).—5 : 6 : 7 : 8-Tetrahydro-4-(5 : 6 : 7 : 8-tetrahydro-2-naphthyl)phenanthrene-2 : 3-dicarboxylic anhydride (0·2 g.) in nitrobenzene (10 c.c.) was treated with anhydrous aluminium chloride (0·3 g.). After 1 hr. at room temperature and ½ hr. at 50° the solution was poured into dilute hydrochloric acid and steam distilled, and the residue was recrystallised from benzene, to give the *keto-acid* (0·12 g.) as large red cubes, m. p. 273—274° (Found : C, 81·9; H, 6·0. $C_{26}H_{22}O_3$ requires C, 81·7; H, 5·8%). The keto-acid (*ca.* 70 mg.) was decarboxylated by copper bronze in quinoline for 1 hr. and the product dehydrogenated at 340—360° for 2 hr. with 30% palladium charcoal. This gave 7 : 8-benzonaphtho(2′ : 1′-3 : 4)-fluorenone (V; R = H), m. p. 238—239° (after chromatography in benzene on alumina), undepressed on admixture with the sample previously prepared.

1-2′-*Naphthylanthracene*.—The sodium salt prepared from 5 : 6 : 7 : 8-tetrahydro-1-(5 : 6 : 7 : 8-tetrahydro-2-naphthyl)anthracene-2 : 3-dicarboxylic anhydride (0·5 g.) by concentration in dilute aqueous sodium hydroxide containing ethanol was dehydrogenated by 30% palladium–charcoal (0·2 g.) and copper bronze (2·0 g.) for 3 hr. at 320—360°. The distillate which was formed on dry distillation was chromatographed in benzene on alumina, giving 1-2′-*naphthylanthracene* (30 mg.) as colourless plates from ethanol–benzene, m. p. 142—143° (Found : C, 94·5; H, 5·4. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%). Its solutions had a purple fluorescence. It gave a brick-red 1 : 3 : 5-trinitrobenzene *complex*, m. p. 127—128° (from ethanol–benzene) (Found : N, 7·8. $C_{30}H_{19}O_6N_3$ requires N, 8·1%).

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