*Polycyclic Systems. Part VI.** 8-meso-α-*Naphthanthr*-10-*one and* 2 : 3-8 : 9-*Dibenzoperylene.*

By E. A. Braude, J. S. Fawcett, and A. A. Webb.

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A novel route to certain types of condensed polycyclic benzenoid systems is illustrated by unambiguous syntheses of *meso*-α-naphthanthr-10-one and 2 : 3-8 : 9-dibenzoperylene *via* 1-*o*-tolyl- and 1 : 5-di-*o*-tolyl-anthraquinone.

The light absorption properties of these and related compounds are recorded and discussed.

In two earlier papers (Braude and Fawcett, *J.*, 1951, 3113, 3117), a novel synthesis of phenanthridines and larger polycyclic systems embodying the phenanthridine skeleton was described which involves the cyclisation of Diels–Alder adducts of *o*-nitrophenylbutadiene (I; R = NO_2), with the nitro-group eventually furnishing the ring-nitrogen atom. An analogous route to phenanthrenes and larger polycyclic systems embodying the phenanthrene skeleton can be envisaged, which depends on the cyclisation of adducts of *o*-tolylbutadiene (I; R = Me) (Braude, Jones, and Stern, *J.*, 1947, 1087), with the *o*-methyl group eventually furnishing the 9-carbon atom. In the simplest case, the expected adduct (II; R = Me) of the diene with acraldehyde would be cyclised to give, after de-

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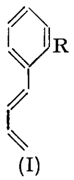
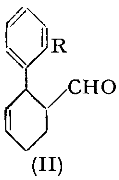
* Part V, *J.*, 1953, 2208.

hydrogenation, phenanthrene itself. However, whereas phenylbutadiene (I; R = H) readily forms an adduct with acraldehyde (Lehmann and Paasche, *Ber.*, 1935, **68**, 1146; Lehmann, 1936, **69**, 631), no reaction could be induced with *o*-tolylbutadiene, even at 200°. Since *o*-nitrophenylbutadiene reacts even more readily than phenylbutadiene (Braude and Fawcett, *loc. cit.*), the inhibiting effect of the *o*-methyl group must be predominantly electronic rather than steric in origin and shows that Diels–Alder addition is retarded by electron-donating substituents in the diene.



(I)



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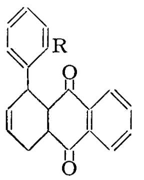

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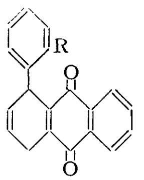

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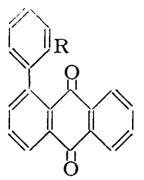
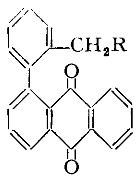


(V)

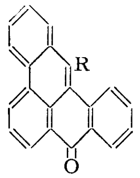
Despite this discouraging result, the possibility of utilising the same approach in other cases of more direct interest was then investigated. In view of their greater reactivity, quinones represent a more suitable type of dienophile. Reaction of phenylbutadiene with naphtha-1 : 4-quinone in the absence of solvent or in hot nitrobenzene is accompanied by complete dehydrogenation, and gives 1-phenylanthraquinone (V; R = H) (Diels, Alder, and Stein, *Ber.*, 1929, **62**, 2337; Weizmann, Bergmann, and Haskelberg, *J.*, 1939, 391; Bergmann, Haskelberg, and Bergmann, *J. Org. Chem.*, 1942, **7**, 303). Reaction in ethanol at room temperature in the presence of a trace of quinol, however, gave mainly the 1 : 4-dihydro-derivative (IV; R = H), and in ethanol at 160—220° a mixture of the latter and the anthraquinone was obtained. *o*-Tolylbutadiene similarly gave 1 : 4-dihydro-1-*o*-tolylanthraquinone (IV; R = Me) and 1-*o*-tolylanthraquinone (V; R = Me) in about 50% total yield, and the dihydro-derivative was quantitatively converted into the fully dehydrogenated product by treatment with oxygen in alcoholic potassium hydroxide. The positions of the two extra hydrogen atoms in the dihydro-derivatives follow from the ultra-violet light absorption which resembles that of naphtha-1 : 4-quinone (see below). The 11 : 12-hydrogen atoms in the original adducts (III) are evidently even more labile than the 1 : 4-hydrogen atoms, in conformity with general experience (cf. Diels and Alder, *loc. cit.*; Fieser, *J. Amer. Chem. Soc.*, 1948, **70**, 3165; Braude and Fawcett, *loc. cit.*; *J.*, 1952, 1528).

The projected conversion of *o*-tolylanthraquinone into *meso*-α-naphthanthr-10-one (VII; R = H) is formally analogous to Scholl's classical synthesis (*Ber.*, 1910, **43**, 346) of pyranthrone dyes from 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl. However, the methyl groups in the latter are exceptionally reactive and attempts to dehydrate *o*-tolylanthraquinone directly by the action of alkali at elevated temperatures yielded mainly unchanged starting material. Other methods of cyclisation were therefore sought and the following successful procedure was developed. Reaction of the quinone with one mol. of *N*-bromosuccinimide gave the *o*-bromomethyl derivative (VI; R = Br) the constitution of which was confirmed by hydrolysis to the hydroxymethyl derivative (VI; R = OH) and oxidation to the carboxylic acid (V; R = CO_2H). Ring-closure of the bromomethyl derivative was first attempted by conversion into the Grignard derivative and internal addition to the carbonyl group, but no reaction with magnesium or lithium could be induced. However, treatment with potassium cyanide in boiling aqueous dioxan resulted in a smooth replacement reaction accompanied by dehydration *in situ* of the resulting cyanomethyl derivative (VI; R = CN) to the cyano-*meso*-α-naphthanthrone (VII; R = CN). This step resembles the intramolecular condensation of benzyl cyanides with quinones in the Hinsberg synthesis of anthracenes (*Ber.*, 1910, **43**, 1360; cf. Moureu, Chovin, and Rivoal, *Bull. Soc. chim.*, 1946, **13**, 106; 1948, **15**, 99; Orchin and Reggel, *J. Amer. Chem. Soc.*, 1951, **73**, 436; Mosby, *ibid.*, 1953, **75**, 3600).

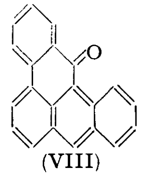
When heated with potassium hydroxide in ethylene glycol, the cyanide (VII; R = CN) underwent hydrolysis and decarboxylation to the naphthanthrone (VII; R = H). The same constitution had previously been assigned by Clar (*Ber.*, 1943, **76**, 609) to a product for which he reported somewhat different physical properties; he obtained it by a series of reactions which could equally have led to the isomeric anthrone (VIII). However, the original specimen, kindly supplied by Dr. Clar, after purification gave no melting-point depression on admixture with our material and a re-determination of the ultra-violet light absorption confirmed that the two substances are, in fact, identical.



(VI)

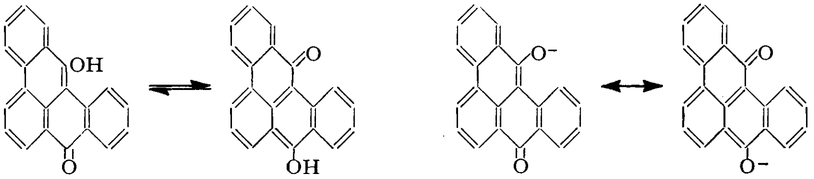


(VII)



(VIII)

Hydrolysis of the cyanide (VII; R = CN) by concentrated sulphuric acid instead of alkali gave the very high-melting hydroxy-derivative (IX). Although nucleophilic substitution in reactive aromatic systems is well known (cf. Bunnett and Zahler, *Chem. Reviews*, 1951, **49**, 273), the replacement of —CN by —OH under *acid* conditions is somewhat unexpected; a good indication of the relatively high lability of cyano-substituents in quinonoid systems is, however, provided by the ready liberation of hydrogen cyanide from dicyanobenzoquinones (Thiele and Günther, *Annalen*, 1906, **349**, 51).* In the present case, attack by the hydrogen sulphate anion SO_4H^-, followed by hydrolysis, is presumably involved. The hydroxyanthrone can exist in two tautomeric forms (IX) and (X); its solutions in alkalis have a deep red colour due to the anion (IX*a*) ⟷ (X*a*) which is stabilised by charge-resonance.



(IX) (X) (IX*a*) (X*a*)

With a view to applying similar methods to the synthesis of larger polycyclic systems, the reactions of phenylbutadiene and *o*-tolylbutadiene with benzoquinone were next examined. When equimolar proportions of diene and quinone were used, only the mono-adducts (XI; R = H and Me) were formed (Braude, Jones, and Stern, *loc. cit.*) which were rearranged by acetic or stronger acid to the 5 : 8-dihydronaphthaquinols (XII).† The quinols are oxidised by nitrous acid to the 5 : 8-dihydronaphthaquinones (XIII) and by chromic acid to the naphthaquinones (XIV) (cf. Fieser, *loc. cit.*). It is of interest that 5 : 8-dihydro-1-*o*-tolylnaphthaquinone (XIII; R = Me) is stable to chromic acid and is evidently not an intermediate in the oxidation of (XII) to (XIV) (cf. Fieser, *loc. cit.*); this means that the dihydrobenzene ring in (XII) is oxidised before the quinol grouping.

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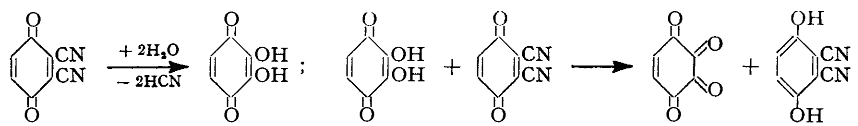
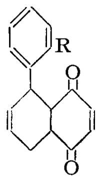
* The course of this interesting reaction, which also yields the corresponding dicyanoquinol, may be represented as follows:



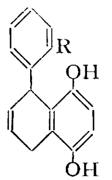
(Not isolated)

† The adduct (XI; R = H) has m. p. 101° (Braude, Jones, and Stern, *loc. cit.*). The compound, m. p. 170°, described by Weizmann, Bergmann, and Haskelberg (*loc. cit.*) as 5-phenyl-5 : 8 : 9 : 10-tetrahydronaphtha-1 : 4-quinone, is the quinol (XII; R = H) formed from the adduct under acidic conditions of isolation.

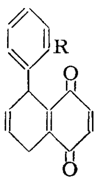
Further reaction of (XIII; R = Me) with *o*-tolylbutadiene in ethanol or nitrobenzene near 200° gave two products, a ditolylanthraquinone, m. p. 277°, and a tetrahydroditolylanthraquinone. The latter was oxidised, by passage of oxygen through its suspension in methanolic potassium hydroxide, to a second ditolylanthraquinone, m. p. 192°. Comparison with other pairs of 1 : 5- and 1 : 8-disubstituted anthraquinones suggested that the higher-melting ditolylanthraquinone is the 1 : 5- (XVIII; R = Me) and the lower-melting the 1 : 8-isomer (XXI; R = Me), and this assignment is confirmed by the reactions described later.



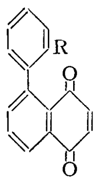
(XI)



(XII)

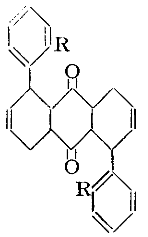


(XIII)



(XIV)

Since the yields of ditolylanthraquinones, particularly of (XVIII), obtained by stepwise addition were very low, the reaction of benzoquinone with two molar proportions of diene was studied. With phenylbutadiene in ethanol, the diadduct (XV; R = H) was formed, while in the presence of acetic acid a 50% yield of a hexahydrodiphenylanthraquinone was obtained, which is formulated as (XVI; R = H) on the basis of its ultraviolet light absorption which resembles that of 5 : 8-dihydro-5-phenyl-1 : 4-naphthaquinone (Braude, Jones, and Stern, *J.*, 1947, 1087). In boiling ethanol and in boiling benzene, the yield of adduct (XV; R = H) is much reduced, and some dehydrogenation also occurs; the marked temperature effect suggests that the addition is reversible under these conditions. Oxidation of the adduct (XV; R = H), or its partial dehydrogenation products, with oxygen and alcoholic potassium hydroxide gave 1 : 5-diphenylanthraquinone (XVIII; R = H) previously prepared by Bergmann *et al.* (*loc. cit.*) by conducting the addition reaction in boiling nitrobenzene. The formulation of the quinone as (XVIII; R = H) rather than (XXI; R = H) is based on the high melting point, but, in contrast to several other cases (cf. Diels and Alder, *loc. cit.*; Braude and Fawcett, *loc. cit.*; and below), none of the 1 : 8-isomer was obtained.



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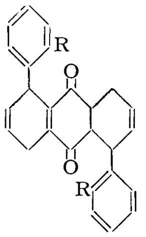
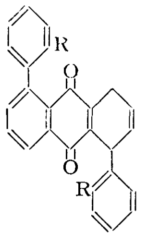
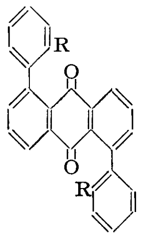


(XVI)

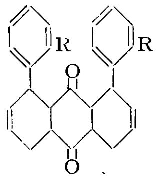


(XVII)

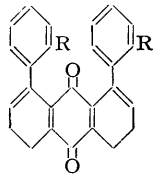


(XVIII)

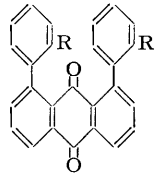
The course of the diaddition of *o*-tolylbutadiene to benzoquinone proved to be remarkably sensitive to the experimental conditions. Depending on the solvent and temperature and on the presence of acids, oxidants or anti-oxidants, the 1 : 5- and 1 : 8-adducts (XV and XIX; R = Me), the two di-*o*-tolylanthraquinones (XVIII and XXI; R = Me), and a variety of intermediate dehydrogenation products (*e.g.*, XVII and XX; R = Me) were obtained; these products were separated by fractional crystallisation. The results do not fall into any well-defined pattern; thus, in ethanol 1 : 5-addition predominated at room temperature and at 170°, but only the 1 : 8-isomer was obtained at 80°, while in nitrobenzene at 100° the product varied from experiment to experiment. These irregularities probably arise from the reversibility of the addition reactions, coupled with a varying ease of dehydrogenation of the different adducts. It was found, however, that trichloroacetic acid which has been reported to catalyse Diels–Alder reactions (Wassermann, *J.*, 1942, 618, 623), and methylene-blue which is a polymerisation inhibitor (Flaig, *Annalen*, 1950, **568**, 1), had a marked beneficial effect and by carrying out the reaction in the presence of these addenda in nitrobenzene, first at 150°, and then at 200°, 1 : 5-ditolylanthraquinone (XVIII; R = Me) was consistently obtained. The dehydrogenation mostly takes place at the higher temperature and the formation of water (from the reduction of nitrobenzene to aniline) can be clearly discerned. Even so, the yield of the anthraquinone is only 10%, much lower than with phenylbutadiene.



(XIX)



(XX)

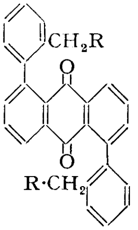


(XXI)

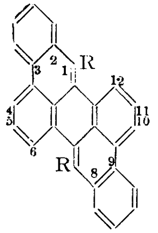
The double cyclisation of 1 : 5-di-*o*-tolylanthraquinone by a procedure analogous to that employed for 1-*o*-tolylanthraquinone presented no undue difficulty. Reaction with *N*-bromosuccinimide in the presence of benzoyl peroxide gave the dibromo-derivative (XXII; R = Br) which was converted by potassium cyanide in aqueous dioxan into the dicyanodibenzoperylene (XXIII; R = CN). Alkaline hydrolysis of the dicyanide at 180° afforded 2 : 3-8 : 9-dibenzoperylene (XXIII; R = H) in an overall yield of 25% based on ditolylanthraquinone. As would be expected, dibenzoperylene and its two derivatives are all high-melting substances which exhibit beautiful fluorescence in extremely dilute solutions.

It is interesting that 2 : 3-8 : 9-dibenzoperylene forms a sesquipicrate, whereas perylene forms a mono- and a di-picrate (Brass and Tengler, *Ber.*, 1931, **64**, 1650; Morgan and Mitchell, *J.*, 1935, 536). Adducts of this type containing fractional ratios of the two components appear to be rare, though a sesquistyphnate of pyrene has been reported by Shinomiya (*Bull. Chem. Soc. Japan*, 1940, **15**, 259; *Chem. Zentr.*, 1940, II, 3168).

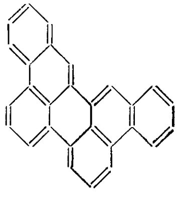
Two dibenzoperylenes which could have the structure (XXIII; R = H) have previously been synthesized, one by the fusion of 9-bromophenanthrene with aluminium trichloride (Clar, *Ber.*, 1932, **65**, 846; Ioffé, *Trudvi Leningrad Khim. Technol. Inst.*, 1934, **1**, 116; *Chem. Abs.*, 1935, **29**, 7969) and the other by a similar fusion of 1 : 1′-diphenanthryl (Ioffé, *loc. cit.*) and 9 : 9′-diphenanthryl (Zinke, Ziegler, *et al.*, *Ber.*, 1941, **74**, 115; *Monatsh.*, 1951, **82**, 645). The two hydrocarbons have similar, though mutually depressed, melting points, and their structures have given rise to some controversy; the courses of the high-temperature fusion reactions are ambiguous and the differences between the spectral properties of the products are too small to allow of a definite assignment (Schauenstein and Bürgermeister, *Ber.*, 1943, **76**, 205). Clar arbitrarily assumed his hydrocarbon to be 2 : 3-10 : 11-dibenzoperylene (XXIV), whereas subsequent workers favoured structure (XXIII; R = H). A comparison of the physical properties of the hydrocarbons with those of 2 : 3-8 : 9-dibenzoperylene obtained by the unambiguous synthesis now described, shows that Clar's product does, in fact, have this structure (XXIII; R = H).



(XXII)



(XXIII)


(XXIV)

Light Absorption Data.—The diene-quinone adducts (III), (XV), and (XIX) exhibit ultra-violet absorption due only to the isolated phenyl or substituted phenyl groups. Data for the 1 : 4-dihydroanthraquinones and anthraquinones produced by dehydrogenation of the adducts are given in the Table, together with those previously obtained (Part II, *J.*, 1951, 3117; Part IV, *J.*, 1952, 1528) for the corresponding methoxy- and nitro-derivatives. The 1-aryl-1 : 4-dihydroanthraquinones (IV) absorb very similarly to naphthaquinone; there is little indication of significant interaction between the unconjugated aryl and the quinone chromophores in this system (cf. Braude, *J.*, 1949, 1902). Similarly, the absorption of 1-arylnaphthaquinones, and of 1-aryl- and 1 : 5- or 1 : 8-diarylanthraquinones, closely resembles that of the unsubstituted quinones, despite the fact that the aryl substituents are here attached directly to the chromophoric system. The absence of effective spectral interaction in this system must be ascribed to steric inhibition, similar to that observed in 1-phenylnaphthalene, 9-phenylanthracene and related examples (cf. Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127; Friedel, Orchin, and Reggel, *ibid.*, 1948, **70**, 199), which opposes the adoption of a uniplanar arrangement by the two conjugated aryl groups. The behaviour of the arylanthraquinones may be contrasted with that of amino-, methoxy-, and nitro-anthraquinones which exhibit the expected substituent effects (Macbeth, Price, and Winzor, *J.*, 1935, 325; Morton and Earlam, *J.*, 1941, 159; Peters and Sumner, *J.*, 1953, 2101).

*Ultra-violet light absorption of aryl-substituted anthraquinone derivatives.**

1 : 4-*Naphthaquinones and* 1 : 4-*dihydroanthraquinones.*

	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å) †	ε
Naphtha-1 : 4-quinone[1]	2460 2560	19,000 13,500	3340	2750	4200	500
(XIV; R = Me) ‡	2450 2520	22,000 21,000	3370	2500	4350	130
(IV; R = H)	2510	22,600	3320	4000	—	—
(IV; R = Me)	2500	20,000	3350	3600	—	—
(IV; R = OMe)[2]	2590 2640	19,000 17,500	—	—	4130	1500
(XVII; R = Me)	2570 2690	35,000 19,500	3380	3900	4130	220

Anthraquinones.

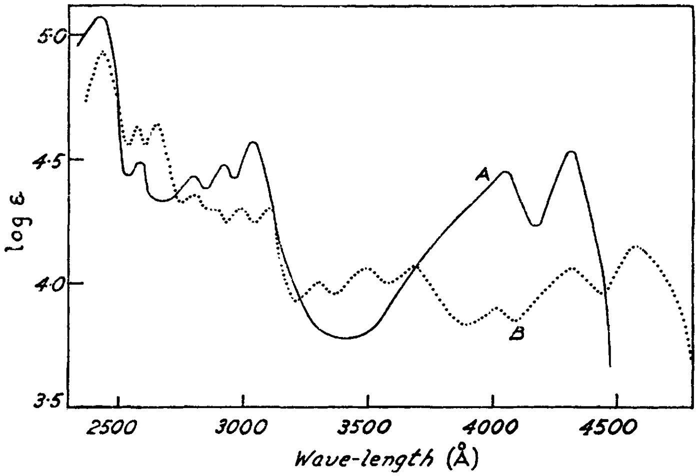
	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å) †	ε
Anthraquinone[3]	2520	51,300	2630 2720	20,400 20,400	3250	5600	4050	890
(V; R = H)	2510	44,500	—	—	3300	4250	—	—
(V; R = Me)	2560	50,000	2700	20,300	3310	5100	—	—
(V; R = OMe)[1]	2440 2495	22,000 24,000	2670	19,000	3350	3300	—	—
(V; R = NO_2)[4]	2570	44,600	—	—	3380	2300	—	—
(XVIII; R = H)	2510 2560	54,000	—	—	3410	6500	4150	430
(XVIII; R = Me)	2560	58,000	2700	25,600	3380	5700	4200	350
(XVIII; R = NO_2)[4]	2510 2580	40,500 47,000	—	—	3300	7000	—	—
(XXI; R = Me)	2570	54,400	2710	26,000	3380	4500	—	—
(XXI; R = NO_2)[4]	2580	46,000	—	—	3150 3300	8000 6300	—	—
(XXII; R = Br)	2570	53,000	—	—	3300	5500	4180	270

* Chloroform solutions. † In many cases, the long wave-length bands appear as shoulders rather than well-defined maxima. ‡ Ethanol solution.

[1] Macbeth, Price, and Winzor, *J.*, 1935, 325 (in ethanol). [2] Braude and Fawcett, *J.*, 1952, 1528. [3] Morton and Earlam, *J.*, 1941, 159. [4] Braude and Fawcett, *J.*, 1951, 3117.

The light absorptions of the naphthanthrones (VII) resemble those of benzanthrone (cf. Clar, *Ber.*, 1932, **65**, 852) and the spectral properties of both the naphthanthrone and dibenzoperylene (see figure) are almost identical with those of some of their aza-analogues (Part II, *loc. cit.*). The fact that replacement of –CH= by –N= in aromatic systems has little effect on electronic spectra is well established (Braude, *Ann. Reports*, 1945, **42**, 108) and a similar correspondence has been observed in many other cases (cf. Barany, Braude, and Pianka, *J.*, 1949, 1898; Albert, Brown, and Cheeseman, *J.*, 1951, 474; Clemo and Felton, *J.*, 1951, 671; Badger, Pearce, and Pettit, *J.*, 1951, 3199; Clemo and Mishra, *J.*, 1953, 192). Cyano substituents enhance the vibrational structure of the ultra-violet bands of both *meso*-naphthanthrone and dibenzoperylene, but the usually observed bathochromic effect is confined to the longest wave-length band of dibenzoperylene.

Light absorption of 2 : 3-8 : 9-*dibenzoperylene* (*A*) *and* 1 : 7-*dicyano*-2 : 3-8 : 9-*dibenzoperylene* (*B*) *in chloroform.*



EXPERIMENTAL

M. p.s marked K were determined on a Kofler block and are corrected. Analytical data were determined in the microanalytical laboratory of this Department (Mr. F. H. Oliver and staff). Light-absorption data, which are only given when not included in the Table, were determined by Mrs. I. A. Boston, using a photographic Hilger-Spekker instrument. Many of the substances described are highly fluorescent and the spectrographic technique employed was designed to minimise the effects of secondary emission (Braude, Fawcett, and Timmons, *J.*, 1950, 1019).

Addition reactions with phenylbutadiene.

1-*Phenylbuta*-1 : 3-*diene*.—This was prepared from cinnamaldehyde (Braude, Jones, and Stern, *J.*, 1947, 1087; Grummitt and Becker, *Org. Synth.*, 1950, **30**, 75) or, more conveniently, from crotonaldehyde. The freshly distilled aldehyde (88 g.) in ether (50 ml.) was added to a stirred solution of phenylmagnesium bromide (from Mg, 24 g., and bromobenzene, 159 g.) in ether (500 ml.) during 1 hr. at 0° (cf. Braude, Jones, and Stern, *J.*, 1946, 396). Stirring was continued for 2 hr. at room temperature and the solution was then cooled again to 0° and excess of saturated aqueous ammonium chloride was added. The ethereal layer was dried (Na_2SO_4) and the solvent removed under reduced pressure. The crude 3-methyl-1-phenylallyl alcohol thus obtained was heated with anhydrous potassium hydrogen sulphate (10 g.) for 30 min. at 100°. The water formed was removed at 10 mm. and the product distilled, giving the diene (96 g., 74%), b. p. 67°/1 mm., n_D^{24} 1·6095, which solidified at 0° and then had m. p. 4°.

Addition to 1 : 4-*Naphthaquinone*.—(*a*) Diene (1 g.), naphthaquinone (1 g., prepared from naphthalene by the method of Braude and Fawcett, *J.*, 1951, 3117; *Org. Synth.*, 1953, **33**, 50), ethanol (5 ml.), and a trace of quinol were shaken for 4 days at room temperature. The product was filtered off, washed with cold methanol, and crystallised from ethanol, giving 1 : 4-*dihydro*-1-*phenylanthraquinone* (IV; R = H) (0·8 g.) as yellow needles, m. p. 139° (Found: C, 83·9; H, 5·0. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%).

(*b*) The diene (1 g.), the quinone (1 g.), ethanol (10 ml.), acetic acid (0·5 ml.), and a trace of quinol were heated for 12 hr. in a sealed tube at 200—220°. On cooling, 1-phenylanthraquinone (0·3 g.) was deposited which was filtered off and crystallised from ethyl acetate in yellow needles, m. p. 176° (Diels, Alder, and Stein, *Ber.*, 1929, **62**, 2337, give m. p. 177—178°). The filtrate, on being kept overnight, deposited 1 : 4-dihydro-1-phenylanthraquinone (0·65 g.), m. p. 139°.

Diaddition to 1 : 4-*Benzoquinone*.—(*a*) Diene (3 g.), quinone (1 g.), ethanol (10 ml.), and benzoyl peroxide (0·1 g.) were heated under reflux for 24 hr. On cooling, 1 : 4 : 5 : 8 : 11 : 12 : 13 : 14-octahydro-1 : 5-diphenylanthraquinone (XV; R = H) (0·3 g.) separated, which crystallised from ethyl acetate in fine colourless needles, m. p. 235° (Found : C, 84·4; H, 6·7. Calc. for $C_{26}H_{24}O_2$, C, 84·75; H, 6·6%) (Weizmann, Bergmann, and Haskelberg, *J.*, 1939, 396, give m. p. 230°). Light absorption in chloroform : $\lambda_{max.}$ 2580 Å, ε 980. The same product, though less pure, was obtained by refluxing the reactants in benzene for 1 hr., removing the solvent under reduced pressure, and adding ethanol.

The octahydroanthraquinone was suspended in a hot 1% solution of potassium hydroxide in ethanol, and oxygen was bubbled through it for a few minutes. This gave 1 : 5-diphenylanthraquinone, m. p. 345° (Bergmann *et al.*, *J.*, 1939, 391; *J. Org. Chem.*, 1942, **7**, 303, give m. p. 355°).

(*b*) Diene (2·4 g.), quinone (1 g.), ethanol (5 ml.), acetic acid (1 ml.), and quinol were shaken for 3 days at room temperature. The product which had separated was filtered off and crystallised from ethyl acetate, giving 1 : 4 : 5 : 8 : 11 : 12-*hexahydro*-1 : 5-*diphenylanthraquinone* (XVI; R = H) (1·1 g.) as very pale yellow needles, m. p. 185—186° (Found : C, 85·0; H, 6·1. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·05%). Light absorption in chloroform : $\lambda_{max.}$ 2690 (ε 5000), 2800 (ε 5000), 2910 (ε 3000), and 3630 Å (ε 200). Braude, Jones, and Stern (*loc. cit.*, 1947) give $\lambda_{max.}$ 2500 (ε 1450), 3640 Å (ε 53), etc., for 5 : 8-dihydro-5-phenylnaphthaquinone.

Oxidation of the hexahydroanthraquinone in hot ethanolic potassium hydroxide as above gave 1 : 5-diphenylanthraquinone, m. p. 345°.

Addition reactions with o-*tolylbutadiene.*

1-o-*Tolylbuta*-1 : 3-*diene*.—(*a*) This was best prepared from crotonaldehyde (1 mol.) and *o*-bromotoluene (1 mol.) as described for phenylbutadiene. The yield of diene, b. p. 82°/0·1 mm., n_D^{19} 1·5993, was 55—65% (Braude, Jones, and Stern, *loc. cit.*, 1947, give b. p. 37°/0·01 mm., n_D^{17} 1·6008). Rapid distillation and the addition of methylene-blue to inhibit polymerisation were advantageous.

(*b*) A warm solution of *o*-toluidine (214 g.) in 8M-hydrochloric acid was chilled and the fine crystalline suspension thus obtained was diazotised by addition of sodium nitrite (140 g.) in water (200 ml.) during 1·5 hr. at 0°. The resulting ice-cold solution was added during 2 hr. to a stirred mixture of butadiene (200 ml.), acetone (1·5 l.), water (300 ml.), sodium acetate (160 g.), and cupric chloride (60 g.) at −10°. Stirring was continued overnight at room temperature and the oily layer was then extracted with ether, washed with water, and dried (Na_2SO_4). Distillation gave 1-*chloro*-4-o-*tolylbut*-2-*ene* (213 g.), b. p. 72°/10^{-2} mm., n_D^{20} 1·5422 (Found : C, 73·8; H, 7·5; Cl, 18·0. $C_{11}H_{13}Cl$ requires C, 73·1; H, 7·2; Cl, 19·6%).

The chlorobutene (60 g.) was added to ethanol (1 l.) and potassium hydroxide (50 g.). No reaction occurred at room temperature. The solution was refluxed for 30 min. and then diluted with water and extracted with ether. Fractionation gave (i) *o*-tolylbutadiene (10 g.), b. p. 68°/1 mm., n_D^{16} 1·5960, and (ii) 1-*ethoxy*-4-o-*tolylbut*-2-*ene* (30 g.), b. p. 91°/1 mm., n_D^{18} 1·5250 (Found : C, 82·3; H, 9·3; OEt, 23·6. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5; OEt, 23·7%).

(*c*) *o*-Bromomethyltoluene (148 g.; Atkinson and Thorpe, *J.*, 1907, **91**, 1695) in ether (300 ml.) was added to magnesium (20 g.) in ether (400 ml.), and the mixture stirred for 1 hr. Freshly distilled acraldehyde (45 g.) in ether (40 ml.) was added slowly at room temperature. After a further 2 hours' stirring excess of saturated aqueous ammonium chloride was added, the ethereal layer was separated and evaporated, and the viscous residue was distilled at 10^{-4} mm. 2 : 2′-Dimethyldibenzyl sublimed first and crystallised from pentane in colourless plates, m. p. 68° (Found : C, 91·3; H, 8·5. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%) (Baker, Banks, Lyon, and Mann, *J.*, 1945, 27, give m. p. 66·5°). This was followed by a small quantity of 1-*o*-tolylbut-3-en-2-ol which was dehydrated to 1-*o*-tolylbutadiene by distillation from potassium hydrogen sulphate.

Addition to Naphthaquinone.—(*a*) Diene (4 g.), quinone (3 g.), ethanol (20 ml.), and a trace of quinol were shaken for 48 hr. at room temperature. The dark blue product was filtered off and boiled with methanol. Recrystallisation from ethyl acetate gave 1 : 4-*dihydro*-1-o-*tolylanthra*-9 : 10-*quinone* (IV; R = Me) (3·7 g.) as yellow needles, m. p. 162° (Found : C, 84·0; H, 5·5. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·4%).

The dihydroquinone (1 g.) was suspended in hot 10% ethanolic potassium hydroxide, and oxygen was bubbled through the mixture for a few minutes. On dilution with water, 1-o-*tolylanthra*-9 : 10-*quinone* (V; R = Me) (0·9 g.) separated, which crystallised from ethanol in fine yellow needles, m. p. 149° (Found : C, 84·3; H, 4·8. $C_{21}H_{14}O_2$ requires C, 84·5; H, 4·7%).

(*b*) Diene (4 g.), quinone (3 g.), ethanol (20 ml.), and acetic acid (0·5 ml.) were heated in a sealed tube for 14 hr. at 180°. A small quantity of an insoluble green product was filtered off which, after crystallisation from nitrobenzene, had m. p. 380—390° (Found: C, 78·6; H, 3·0. Calc. for $C_{30}H_{14}O_5$: C, 79·3; H, 3·1%) and appears to be identical with a self-condensation product of naphthaquinone previously isolated by Pummerer and his co-workers (*Ber.*, 1937, **70**, 2281; 1938, **71**, 2569; 1939, **72**, 1623) and formulated by them as the anhydroquinhydrone of triphthaloylbenzene. The cooled solution slowly deposited 1-*o*-tolylanthraquinone (1·5 g.), m. p. 149°, and, after partial evaporation, 1 : 4-dihydro-1-*o*-tolylanthraquinone (1·6 g.), m. p. 162°, undepressed on admixture with the specimens obtained as under (*a*).

Monoaddition to Benzoquinone.—(*a*) Diene (6 g.), quinone (4 g.), and benzene (20 ml.) were refluxed for 30 min. Partial evaporation gave 5 : 8 : 9 : 10-tetrahydro-5-*o*-tolylnaphthaquinone (5 g.) which crystallised from light petroleum (b. p. 80—100°) in pale yellow plates, m. p. 93° (Braude, Jones, and Stern, *loc. cit.*, 1947, give m. p. 93—95°).

The tetrahydroquinone (2 g.) was dissolved in acetic acid (20 ml.) at 100°. Sodium nitrite (2 g.) in water (3 g.) was added to the hot solution. On cooling and dilution with water (10 ml.), 5 : 8-*dihydro*-5-o-*tolylnaphtha*-1 : 4-*quinone* (XIII; R = Me) (1·8 g.) separated, which crystallised from ethanol in yellow prisms, m. p. 123—124° (Found: C, 81·3; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

The dihydronaphthaquinone was recovered unchanged after treatment with sodium dichromate in sulphuric and acetic acid for ½ hr. at 60° or 100°.

(*b*) Diene (4 g.), quinone (6 g.), benzene (20 ml.), trichloroacetic acid (50 mg.), and methylene-blue (10 mg.) were heated under reflux for 2 hr. The benzene was removed under reduced pressure and the residue was washed with a little ether, boiled with methanol, alumina, and charcoal, and then crystallised from aqueous methanol, giving 5 : 8-*dihydro*-5-o-*tolylnaphtha*-1 : 4-*quinol* (XII; R = Me) (4 g.), m. p. 168° (Found: C, 80·8; H, 6·6. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%).

To the dihydronaphthaquinol (2 g.) in acetic acid (20 ml.), sodium dichromate (2 g.) in 4N-sulphuric acid (5 ml.) was added slowly and the mixture then kept at 100° for 20 min. and finally cooled. Water was added and the product which separated was crystallised from aqueous methanol, giving 5-o-*tolylnaphtha*-1 : 4-*quinone* (XIV; R = Me) as yellow needles, m. p. 114—115° (Found: C, 82·0; H, 4·9. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·9%).

Addition to 5 : 8-*Dihydro*-5-o-*tolylnaphthaquinone.*—Diene (1 g.), quinone (1 g.), and ethanol (10 ml.) were heated in a sealed tube at 200° for 18 hr. On cooling, 1 : 5-di-*o*-tolylanthraquinone (0·15 g.), m. p. 278° (K), and 1 : 4 : 5 : 8-tetrahydro-1 : 8-di-*o*-tolylanthraquinone (0·1 g.), m. p. 218°, separated. Both m. p.s were undepressed on admixture with the authentic specimens described below.

A similar result was obtained by reaction in nitrobenzene at 190° for 1 hr.

Diaddition to Benzoquinone.—(*a*) Diene (2·8 g.), quinone (0·75 g.), and ethanol were shaken for 4 days at room temperature. The product was filtered off, washed with a little ethanol, and crystallised from ethyl acetate, giving 1 : 4 : 5 : 8 : 9 : 10 : 11 : 12-*octahydro*-1 : 5-*di*-o-*tolylanthra*-9 : 10-*quinone* (XV; R = Me) (0·3 g.) as colourless, hexagonal plates, m. p. 221—223° (Found: C, 84·7; H, 7·3. $C_{28}H_{28}O_2$ requires C, 84·8; H, 7·1%). Light absorption in chloroform: $\lambda_{max.}$ 2640 Å; ε 550. The same product in similar yield was usually obtained in the presence of a little acetic acid or quinol, but in one experiment, in the presence of quinol, 1 : 4 : 5 : 8-tetrahydro-1 : 8-di-*o*-tolylanthraquinone (see below, *b*), m. p. 219°, was isolated instead.

The octahydroanthraquinone (0·20 g.) was suspended in a boiling solution of potassium hydroxide (1 g.) in ethanol (10 ml.), and a rapid stream of oxygen was passed through the whole for 10 min. On cooling and dilution with water, 1 : 5-*di*-o-*tolylanthra*-9 : 10-*quinone* (XVIII; R = Me) (0·18 g.) separated, which was sublimed at 10^{-4} mm. and formed yellow plates, m. p. 278° (K) (Found: C, 86·8; H, 5·4. $C_{28}H_{20}O_2$ requires C, 86·6; H, 5·2%).

(*b*) Diene (2·8 g.), quinone (1 g.), and ethanol (5 ml.) were refluxed for 4 hr. On cooling, 3 : 4 : 5 : 6(?)-*tetrahydro*-1 : 8-*di*-o-*tolylanthra*-9 : 10-*quinone* (XX; R = Me) (0·3 g.) separated, which crystallised from ethyl acetate in orange needles, m. p. 219—221° (Found: C, 85·7; H, 6·4. $C_{28}H_{24}O_2$ requires C, 85·7; H, 6·2%). Light absorption in chloroform; $\lambda_{max.}$ 2650 (ε 10,000) and 3040 Å (ε 3600).

Oxidation of the tetrahydroanthraquinone (0·20 g.) in ethanolic potassium hydroxide as under (*a*) gave 1 : 8-*di*-o-*tolylanthra*-9 : 10-*quinone* (XXI; R = Me) (0·19 g.), which after sublimation formed yellow plates, m. p. 192° (Found: C, 86·1; H, 5·3. $C_{28}H_{20}O_2$ requires C, 86·6; H, 5·2%).

(*c*) Diene (2·8 g.), quinone (1 g.), and ethanol (10 ml.) were heated in a sealed tube at 170°

for 18 hr. The product was oxidised as above, giving 1 : 5-di-*o*-tolylanthraquinone (0·3 g.), m. p. 278° (K).

(*d*) Diene (4 g.), quinone (1 g.), nitrobenzene (10 ml.), and methylene-blue (5 mg.) were kept at 90° for 20 hr. and then refluxed for 10 min. The solvent was removed at 100°/1 mm. and the residue refluxed with a little ethanol for a few minutes. The crystalline, yellow product was recrystallised from xylene, giving 1 : 5-di-*o*-tolylanthraquinone (0·3 g.), m. p. 278°.

The same result was obtained on heating the mixture at 135° for 45 hr., but in one experiment in which acetic acid (2 ml.) was added, only tetrahydro-1 : 8-di-*o*-tolylanthraquinone (0·2 g.), m. p. 219°, was isolated after 18 hr. at 90°.

(*e*) Diene (3·4 g.), quinone (1 g.), nitrobenzene (10 ml.), and a trace of quinol were heated under reflux for 10 min. and then kept at 100° for 4 hr. Most of the nitrobenzene was removed at 100°/1 mm. and the residue diluted with ethanol. The product which separated is formulated as 1 : 4-*dihydro*-1 : 5-*di*-o-*tolylanthra*-9 : 10-*quinone* (XVII; R = Me) and sublimed in *vacuo*, giving fine yellow needles, m. p. 258° (Found : C, 86·1; H, 5·8. $C_{28}H_{22}O_2$ requires C, 86·1; H, 5·7%).

(*f*) Diene (10 g.), quinone (3 g.), nitrobenzene (50 ml.), trichloroacetic acid (0·5 g.), and methylene-blue (100 mg.) were heated to 150° in an oil-bath. Additional small portions of methylene-blue were added from time to time when the green colour of the solution began to change to brown. After 3 hr. at 150°, the temperature was raised to 200° for 1 hr. Working-up as under (*d*) and crystallisation from xylene–nitrobenzene containing a few drops of concentrated hydrochloric acid gave 1 : 5-di-*o*-tolylanthraquinone (1·0 g.), m. p. 277°. This is the most satisfactory procedure for the preparation of this compound and gave consistent results in several experiments.

meso-α-*Naphthanthrone* [*naphtha*(1′ : 2′ : 3′-1 : 13 : 9)*anthrone*].

Attempted Direct Cyclisation of 1-o-*Tolylanthraquinone*.—The quinone (2 g.), ethanol (15 ml.), and potassium hydroxide were heated in a sealed tube at 150° for 12 hr. On dilution with water, only unchanged quinone was recovered. The same result was obtained at 200°, with ethylene glycol as solvent.

1-o-*Bromomethylphenylanthra*-9 : 10-*quinone* (VI; R = Br).—1-*o*-Tolylanthraquinone (2 g.), *N*-bromosuccinimide (1·3 g.), carbon tetrachloride (20 ml.), and benzoyl peroxide (10 mg.) were heated under reflux for 12 hr. After filtration, the solution was diluted with methanol. The 1-o-*bromomethylphenylanthra*-9 : 10-*quinone* (2·2 g.) which separated crystallised from ethyl acetate as yellow plates, m. p. 181—182° (Found: C, 67·2; H, 3·8; Br, 21·1. $C_{21}H_{13}O_2Br$ requires C, 66·9; H, 3·5; Br, 21·2%). Light absorption in chloroform : $\lambda_{max.}$ 2520 (ε 51,000), 2560 (ε 56,000), 2730 (ε 21,500), and 3300 Å (ε 6300), $\lambda_{infl.}$ 2780 Å (ε 20,000).

No reaction occurred between the bromide and various forms of " activated " magnesium, or with lithium, in boiling ether–benzene, and unchanged bromide was recovered.

1-o-*Hydroxymethylphenylanthra*-9 : 10-*quinone* (VI; R = OH).—The foregoing bromide (0·35 g.), potassium carbonate (0·1 g.), dioxan (36 ml.), and water (4 ml.) were heated under reflux for 24 hr. Dilution with water, extraction with benzene, and evaporation gave 1-o-*hydroxymethylphenylanthra*-9 : 10-*quinone* (0·25 g.) which separated from light petroleum (b. p. 60—80°) in yellow crystals, m. p. 153° (Found : C, 79·5; H, 4·2. $C_{21}H_{14}O_3$ requires C, 80·2; H, 4·5%). Light absorption in chloroform : $\lambda_{max.}$ 2560 (ε 51,000), 2730 (ε 20,500), and 3320 Å (ε 5300).

1-o-*Carboxyphenylanthra*-9 : 10-*quinone* (V; R = CO_2H).—The foregoing hydroxymethyl compound (0·24 g.) in acetone (5 ml.) was oxidised by the addition of potassium permanganate (0·5 g.) in aqueous sodium carbonate (8 ml.). The mixture was stirred for 30 min., then filtered and acidified with hydrochloric acid. The precipitated *acid* (0·15 g.) crystallised from ethanol in yellow needles, m. p. 212° (Found : C, 77·3; H, 4·0. $C_{21}H_{12}O_4$ requires C, 76·8; H, 3·7%).

4′-*Cyanonaphtha*(1′ : 2′ : 3′-1 : 13 : 9)*anthrone* (VII; R = CN).—1-*o*-Bromomethylphenylanthraquinone (2 g.), potassium cyanide (0·6 g.), dioxan (180 ml.), and water (20 ml.) were heated under reflux for 18 hr. On cooling and addition of water (50 ml.) the *cyanonaphthanthrone* (1·6 g.) separated, which crystallised from dioxan in fine yellow needles, m. p. 261—262° (Found : C, 86·7; H, 3·7; N, 4·4. $C_{22}H_{11}ON$ requires C, 86·6; H, 3·6; N, 4·6%). Light absorption in chloroform : $\lambda_{max.}$ 2440 (ε 49,000), 2510 (ε 47,000), 2670 (ε 30,500), and 3900 Å (ε 20,000); $\lambda_{infl.}$ 2930 (ε 12,000), 3080 (ε 10,500), and 3160 Å (ε 10,000).

meso-α-*Naphthanthrone* (VII; R = H).—The foregoing cyano-derivative (1 g.), ethylene glycol (5 ml.), and potassium hydroxide (2 g.) were kept at 160° in a copper flask for 4 hr., then cooled. 50% Sulphuric acid (20 ml.) was slowly added and the precipitate was filtered off, washed, and dried. Crystallisation from dioxan gave the naphthanthrone (0·8 g.) as yellow needles,

m. p. 232°, 240° (K) (Found: C, 89·9; H, 4·4. Calc. for $C_{21}H_{12}O$: C, 90·0; H, 4·3%). The sample described (*Ber.*, 1943, **76**, 609) and kindly supplied by Dr. Clar had m. p. 226°, 237° (K), mixed m. p. 226°. Both samples showed identical light absorption in ethanol: $\lambda_{max.}$ 2410 (ε 53,000), 2650 (ε 28,000), 3020 (ε 22,500), and 3950 Å (ε 14,500); $\lambda_{infl.}$ 2890 (ε 20,500) and 3120 Å (ε 17,500) (for full curve, see Braude and Fawcett, *J.*, 1951, 3119) (Clar, *loc. cit.*, gives $\lambda_{max.}$ 2410, 2700, 2900, 3030, 3180, and 4040 Å).

4′-Hydroxynaphtha(1′ : 2′ : 3′-1 : 13 : 9)*anthrone* (VII; R = OH).—The above cyano-derivative (1 g.) and concentrated sulphuric acid (10 ml.) were heated to 170° for 4 hr. The mixture was poured on ice and made alkaline with aqueous sodium hydroxide. The resulting deep-red solution was filtered and acidified with sulphuric acid. The flocculent, yellow precipitate was filtered off, washed, dried, and sublimed at 280° in *vacuo*, giving fine yellow needles of the *4′-hydroxy-ketone* (0·25 g.) (Found: C, 85·6; H, 4·3. $C_{21}H_{12}O_2$ requires C, 85·1; H, 4·1%). It had no definite m. p. and was practically insoluble in common organic solvents.

2 : 3-8 : 9-*Dibenzoperylene*.

1 : 5-*Di*-(o-*bromomethylphenyl*)*anthra*-9 : 10-*quinone* (XXII; R = Br).—1 : 5-Di-*o*-tolylanthraquinone (1·16 g.), *N*-bromosuccinimide (1·60 g., freshly crystallised and dried; cf. Chapman and Williams, *J.*, 1952, 5044; Kooyman, Helden, and Bickel, *Proc. K. Ned. Akad. Wet.*, 1953, *B*, **56**, 75), carbon tetrachloride (25 ml.), chloroform (5 ml.), and benzoyl peroxide (40 mg.) were heated under reflux with exclusion of moisture. The solution became first deep-red and later light yellow. After 6 hr. succinimide (0·76 g., 84%), m. p. 126—128°, was filtered off and the solvent removed under reduced pressure, leaving the *dibromo*-derivative (1·05 g.). Recrystallised from benzene–light petroleum (b. p. 60—80°) it formed yellow needles, m. p. 184—187° (Found: Br, 30·4. $C_{28}H_{18}O_2Br_2$ requires Br, 29·3%).

1 : 7-*Dicyano*-2 : 3-8 : 9-*dibenzoperylene* (XXIII; R = CN).—The foregoing crude dibromo-derivative was dissolved in dioxan (45 ml.), and potassium cyanide (1·5 g.) in water (5 ml.) was added. The clear solution was then heated under gentle reflux for 12 hr. The solvents were removed under reduced pressure and the residue was washed with water. A portion of the crude *dicyanodibenzoperylene* (0·9 g.) thus obtained was crystallised from nitrobenzene, giving orange needles, m. p. $>$360° (Found: N, 6·3. $C_{30}H_{14}N_2$ requires N, 7·0%). Light absorption in chloroform: $\lambda_{max.}$ 2430 (ε 84,000), 2560 (ε 44,000), 2650 (ε 44,000), 2800 (ε 23,000), 2980 (ε 20,000), 3100 (ε 20,000), 3300 (ε 10,000), 3480 (ε 12,000), 3670 (ε 12,000)· 4020 (ε 8000), 4330 (ε 12,000), and 4560 Å (ε 14,000) (see also curve, p. 1055). Dilute solutions of the dinitrile in chloroform, dioxan, or nitrobenzene were yellow-green and exhibited an intense green fluorescence.

2 : 3-8 : 9-*Dibenzoperylene* (XXIII; R = H).—The foregoing crude dinitrile, ethylene glycol (10 ml.), and potassium hydroxide (3·0 g.) were heated under reflux for 6 hr., during which the colour of the solution changed from intense green to deep-red. The solution was acidified with 50% sulphuric acid, and the yellow-brown precipitate was extracted with boiling methanol in a modified Soxhlet apparatus. On acidification of the red, bright pink-fluorescent methanol solution with sulphuric acid, an amorphous brown product was precipitated.

The methanol-insoluble product was extracted with boiling xylene. The deep-red, green-fluorescent solution was boiled with charcoal, filtered, and concentrated. Addition of ether to the cooled concentrate precipitated golden spangles of the dibenzoperylene (0·25 g.), m. p. 339—342°. Crystallisation from xylene–nitrobenzene gave golden-yellow plates, m. p. 342° (Found: C, 94·8; H, 4·7. $C_{28}H_{16}$ requires C, 95·4; H, 4·6%) (Clar, *Ber.*, 1932, **65**, 846, gives m. p. 343°). Light absorption in chloroform: $\lambda_{max.}$ 2420 (ε 116,000), 2560 (ε 31,000), 2800 (ε 27,000), 2910 (ε 31,000), 3020 (ε 39,000), 4050 (ε 27,000), and 4300 Å (ε 35,000) (see also curve, p. 1055) (Clar, *loc. cit.*, gives $\lambda_{max.}$ 2900, 3020, 3850, 4050, and 4300 Å, log ε 4·6, 4·7, 4·3, 4·6, and 4·6 respectively). Dibenzoperylene is very sparingly soluble in boiling benzene, ether, chloroform, etc., giving orange solutions with a blue fluorescence. Solutions in nitrobenzene are deep red with a blue fluorescence. With concentrated sulphuric acid in the cold, the hydrocarbon gives a green colour changing rapidly to bright purple. It formed a *picrate* which crystallised from xylene in plates, m. p. 239—242° (Found: C, 63·3; H, 3·4; N, 8·6. $2C_{28}H_{16},3C_6H_3O_7N_3$ requires C, 63·8; H, 3·0; N, 9·05%) (Clar, *loc. cit.*, gives m. p. 240°, but no analytical data).

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DEPARTMENT OF ORGANIC CHEMISTRY, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.
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