BENZOLOGUES AND OTHER DERIVATIVES OF PEROPYRENE

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Abstract—Peropyrene (III) was synthesized via the diketone (II) and by reduction of peropyrenequinone (IV). The latter can also be obtained from the diketone (II). 4:4'-Dibenzanthronyl gave 4:4'dibenzanthrenyl (V), the dehydrogenation of which yielded the yellow compound (VI) which displayed thermochomy involving the blue form (VIa). This decomposed to (VII). Condensation of benzanthrone with phosphorus oxychloride gave 4:5,11:12-dibenzoperopyrene (VIII), 4:5,9:10-dibenzoperopyrene (IX), 4:5,8:9-dibenzoperopyrene (X) and 2:3,8:9-dibenzoperopyrene (VII), 5:6,12:13-dibenzoperopyrene (XIV) was synthesized via (XII) and (XIII). A zinc dust melt of 8:8'dibenzanthronyl (XVII) gave 3:4,11:12-dibenzobisanthene (XXI). A mixture of the dibenzanthronyls (XVII), (XVIII) and (XIX) gave 3:4,10:11-dibenzobisanthene (XX) in addition. The dinaphthoperopyrenes (XXIII) and (XXIV) resulted from a zinc dust melt of naphthanthrone (XXII).

WHEN perinaphthone (I) was reduced with aqueous sodium hydroxide solution and zinc dust a colourless product was obtained. It had no phenolic properties and its infra-red spectrum showed a strong carbonyl peak at 1675 cm⁻¹. Condensation of the



F10. 1. Absorption max (Å) and log ε (in parentheses). Peropyrene-3,8-quinone IV in 1,2,4-trichlorobenzene, 5980 (4.66), 5560 (4.48), 4650 (4.24), 4340 (4.11), 3800 (4.04), 3340 (4.20). Dichloroperopyrene in 1,2,4-trichlorobenzene, p: 4570 (4.92), 4280 (4.66), 4030 (4.18); β : 3300 (4.40).

diketone (II) with alcoholic potassium hydroxide gave peropyrene quinone (IV). This quinone was also obtained by condensation of perinaphthone(I) in alcoholic potassium hydroxide. It is described in the patent literature,¹ but has never been characterized as a pure compound. The absorption spectrum is shown in Fig. 1. It is obvious that the condensation of perinaphthone (I) proceeded in an analogous way to the condensation of benzanthrone to violanthrone.⁸ A zinc chloride sodium chloride melt of the diketone (II) gave peropyrene (III). This hydrocarbon was also prepared

¹ Badische Anilin und Soda Fabrik, Ger. Pat. 283066 (1913).

⁸ A. Lüttringhaus and H. Neresheimer, Liebigs Ann. 473, 259 (1929).

in good yield by a zinc dust melt of peropyrene quinone. When the latter was oxidized with chromic acid, an acid was formed which yielded perylene on decarboxylation. This confirms the view that the carbonyl groups are located in the two terminal rings. The above syntheses gave much better yields than the one previously reported.³ 4:4'-Dibenzanthronyl² was smoothly reduced to 4:4'-dibenzanthrenyl (V) with zinc dust, pyridine and acetic acid. For the absorption spectrum see Fig. 2. It could be dehydrogenated with chloranil, nitrobenzene or palladium charcoal in trichlorobenzene



Fig. 2. Absorption max (Å) and log ϵ (in parentheses). Benzanthrene in alcohol, p: 3440 (4·14), 3290 (4·22), 3120 (4·08); 2500 (4·20); β 2280 (4·64). 4:4'-Dibenzanthrenyl V in benzene, p: 3570 (4·54), 3410 (4·52); in alcohol, 2500 (4·50); β 2260 (4·90).

to a yellow compound, probably (VI), which when heated in xylene or nitrobenzene solution changed to a deep blue solution, showing an absorption band at 6000 Å. The colour disappeared again on cooling. The thermochromy could be observed **many** times in xylene solution before the compound was finally transformed into 1:2,9:10-dibenzoperopyrene (violanthrene, VII). This condensation also took place after a short boiling in nitrobenzene. Owing to its sensitivity, the compound (VI) could not be recrystallized in an analytical pure state. However, the assumption of the equilibrium (VI) \sim (VIa) is the most likely explanation for the thermochromy.

When heated with benzene and aluminium chloride, peropyrene (III) gave a phenylperopyrene, which has an absorption spectrum closely related to peropyrene (Fig. 3). The phenyl group is most likely in one of the terminal rings because substitution in the positions 5 and 6 would have produced a new ring on cyclization and a corresponding major alteration in the spectrum. Peropyrene can be oxidized to peropyrene quinone which is identical with the quinone obtained by direct syntheses. Peropyrene does not form an adduct with boiling maleic anhydride and chloranil, but gives a little dichloroperopyrene (Fig. 1). It has therefore no perylene character. Unlike perylene the two central bonds cannot assume single bond character in terms of Kekule structures.⁴ However, peropyrenequinone (IV) is a perylene derivative by

^{*} E. Clar, Ber. Disch. Chem. Ges. 76, 458 (1943).

⁴ D. M. Donaldson, J. M. Robertson and J. G. White, Proc. Roy. Soc. A 220, 311 (1953).

this definition. Accordingly, it forms quite readily an adduct with maleic anhydride, with or without chloranil. This brownish yellow anhydride could not be recrystallized from high boiling solvents because of the dissociation which also took place in an attempt to decarboxylate with soda lime or in quinoline with copper powder. Dissociation was also complete when the adduct was reduced with zinc dust in aqueous alkali. Violanthrone (1:2,9:10-dibenzoperopyrene-3,8-quinone) also gives a dissociable adduct.





















VШ



IX



X

A condensation of two molecules of benzanthrone with phosphorus oxychloride⁵ gave besides the already known yellow 4:5,11:12-dibenzoperopyrene⁶ two hitherto unknown dibenzopyrenes. They can have only the structure of a 1:2,6:7-dibenzoperopyrene (IX) and 1:2,11:12-dibenzopyrene (X). They are not identical with



FIG. 3. Absorption max $(\vec{\Lambda})$ and log ε (in parentheses).

Peropyrene III in alcohol, p: 4365 (5·14), 4100 (4·90), 3860 (4·42), 3660 (3·94), 3480 (3·44); β : 3235 (4·74), 3090 (4·50), 2950 (4·24); β ': 2770 (5·16), 2640 (5·10). Phenylperopyrene in benzene, p: 4530 (5·00), 4260 (4·80), 4030 (4·38); β : 3300 (4·68), 3160 (4·50).



FIG. 4. Absorption max (Å) and log ε (in parentheses). Dibenzoperopyrene m.p. 334–335, (IX or X) in benzene, p: 4820 (4-87), 4530 (4-66), 4200 (4-28), 3960 (3-89); β : 3630 (4-78), 3460 (4-60); β' : 3185 (4-75), 3060 (4-63). Dibenzoperopyrene m.p. 279° (X or IX) in benzene, p: 4720 (4-78), 4450 (4-62), 4180 (4-27); β : 3580 (4-72), 3415 (4-55); β' : 3070 (4-73), 2950 (4-59).

1:2,9:10-dibenzoperopyrene (violanthrene, VII). Their first absorption bands (Fig. 4) are located between the latter and 4:5,11:12-dibenzoperopyrene (VIII, Fig. 5) in accordance with the formulae (IX) and (X).

5:6,12:13-Dibenzoperopyrene (XIV, 2:3,8:9-dibenzooronene) has been synthesized previously in a very complicated way involving numerous intermediate stages.⁷ It could be more easily obtained from 1,4-dimethylanthraquinone which

- ⁴ N. Campbell and A. A. Woodham, J. Chem. Soc. 843 (1952).
- ⁶ E. Clar, Ger. Pat. 621861 (1933); Ber. Dtch. Chem. Ges. 76, 458 (1943).
- ⁷ R. Scholl and K. Meyer, Ber. Dtsch. Chem. Ges. 65, 902 (1932).

yielded the diol (XII) when reacted with o-tolyl-lithium. Reduction with hydriodic acid in acetic acid gave the ditolylanthracene (XIII). Cyclodehydrogenation with palladium charcoal provided dibenzoperopyrene (XIV) in varying yields. Its absorption spectrum shows a striking resemblance with the deep red 1:2,8:9dibenzoperopyrene (isoviolanthrene, (XI), Fig. 6) thus indicating that the two



FIG. 5. Absorption max (Å) and log ε (in parentheses). 4:5,11:12-Dibenzoperopyrene VIII in benzene, p: 4450 (4·86), 4180 (4·73), 3980 (4·36); β : 3480 (5·10), 3320 (4·85), 3165 (4·82), 3110 (4·82), 2960 (4·70). 1:2,9:10-Dibenzoperopyrene (Violanthrene) VII in benzene, p: 4920 (4·91), 4580 (4·60), 4280 (4·28); β : 3820 (4·16), 3610 (4·26), 3430 (4·10); β ': 3275 (4·76), 3140 (4·47), 3000 (4·30).



FIG. 6. Absorption max (Å) and log e (in parentheses). 1:2,8:9-Dibenzoperopyrene XI in 1-methylnaphthalene, p: 5230 (4.90) 4880 (4.65), 4590 (4.34); β : 3640 (4.96). 5:6,12:13-Dibenzoperopyrene XIV in 1-methylnaphthalene, p: 5240 (5.02), 4880 (4.50), 4580 (3.94); β : 3620 (4.54), 3440 (4.16).

double bonds fused to peropyrene in the positions 5:6,12:13 have the same effect as two dienes fused to the positions 1:2,8:9.

3:4,11:12-Dibenzobisanthene (XXI) and 3:4,10:11-dibenzobisanthene (XX) cannot be obtained by a condensation of two molecules of benzanthrone. They were

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synthesized from 6- and 8-chlorobenzanthrone (XV) and (XVI) via the dibenzanthronyls. Pure 8:8'-dibenzanthronyl (XVII) was prepared from 8-chlorobenzanthrone with copper powder in nitrobenzene.⁸ It gave the hitherto unknown pale yellow 3:4,11:12-dibenzobisanthene (XXI) in a zinc dust melt. It has 5 inherent aromatic sextets (marked with circles), i.e. more than any other hydrocarbon consisting of 2 benzanthrene complexes (except (VIII) which is non-planar) and therefore comes nearest to a fully benzenoid hydrocarbon like hexabenzocoronene.⁹ Its p-bands (Fig. 7), accordingly, are the most shifted to the short wave part of the spectrum and it shows a red phosphorescence of long life in solid solution at low temperature.

 W. Bradley, J. Chem. Soc. 1622 (1948).
E. Clar and C. T. Ironside, Proc. Chem. Soc. 150 (1958); E. Clar, C. T. Ironside and M. Zander, J. Chem. Soc. 142 (1959).

The isomer 3:4,10:11-dibenzobisanthene (XX) has only 4 inherent aromatic sextets. It is red and its p-bands are at longer wavelengths (Fig. 7) like the ones of (VII), (IX) and (X), whilst (XI) and (XIV) with only 3 inherent sextets have p-band at the longest wavelength (5150 Å in benzene). 3:4,10:11-dibenzobisanthene (XX) was prepared from a constant melting eutectic mixture of the two chlorobenzan-thrones (XV) and (XVI), which, when treated with copper powder in nitrobenzene,



FIG. 7. Absorption max (Å) and log ε (in parentheses). 3:4,11:12-Dibenzobisanthene XXI in benzene, α : 4660 (3·20), 4475 (3·13), 4380 (3·39); p: 4170 (4·80), 3945 (4·58), 3810 (4·40); β : 3580 (4·73); β' : 2995 (4·45), 2850 (4·25). 3:4,10:11-Dibenzobisanthene XX in benzene, p: 4820 (4·66), 4510 (4·40), 4200 (4·26), 3940 (3·90); 3580 (3·92); β : 3290 (4·92), 3160 (4·66), 3000 (4·40).

gave a mixture of the dibenzanthronyls (XVII), (XVIII) and (XIX). The zinc dust melt yielded a mixture of 3:4,11:12- and 3:4,10:11-dibenzobisanthene (XXI) and (XX) respectively. The former could be enriched in the mixture by chromatography, but not freed from (XXI). The spectrum of pure (XX) was obtained by the subtraction of the absorption curve of (XXI) from that of the mixture.

As could be expected by a comparison of the formulae (XX) and (XXI), the former reacted more readily with maleic anhydride and chloranil and its spectrum gradually disappeared from the mixture in the course of the reaction. However, (XXI) also appears to react to some extent because the decarboxylation of the resulting acids yielded an inseparable mixture of hydrocarbons.



Naphthanthrone (XXII) could be condensed like benzanthrone. This was done in fused zinc chloride with zinc dust. The main product of the reaction was a good

yield of dinaphtho-(7':1',1:13)(1'':7'',6:8)-peropyrene (XXIII). It was identical with the same hydrocarbon obtained by another synthesis.¹⁰ An attempt to condense (XXIII) with bromomaleic anhydride yielded a dibromoderivative of (XXIII).

The chromatography of the reaction product yielded another isomer possibly (XXIV). Its absorption spectrum is recorded in Fig. 8. Although a spectroscopic examination of the crude condensation product indicated the presence of at least two



Fig. 8. Absorption max (Å) and log ε (in parentheses). Dinaphtho-(7':1',1:13) (1":7",6:8)-peropyrene XXIII in benzene, p: 5100 (4:80), 4760 (4:59), 4470 (4:16); β : 3670 (4:92), 3490 (4:58), 3340 (4:26); β ': 3170 (4:72), 3040 (4:61), 2900 (4:59). Dinaphtho-(7':1',1:13) (1":7",9:11)-peropyrene XXIV in benzene, p: 5330 (4:93), 4950 (4:64), 4650 (4:20); β : 3960 (4:48), 3760 (4:42), 3630 (4:37); β ': 3240 (4:60).

more isomers which could be expected in analogy with the condensation of benzanthrone, these hydrocarbons were not eluted from the chromatographic column even after a prolonged extraction.

EXPERIMENTAL[•]

7, 8, 7', 8'-Tetrahydro-3, 3'-diperinaphthonyl (II). Perinaphthenone I (10 g) in hot xylene (50 ml) was added to a boiling mixture of sodium hydroxide (200 ml, 5%) and zinc dust (5 g). The solution became a deep red colour, which faded after 30 min. The xylene was removed by steam distillation and the zinc dust filtered off. Extraction with and the crystallization from xylene gave colourless needles of the diketone (II, 1.5 g) m.p. 256-257". (Found: C, 86-1; H, 5-0 C₂₄H₁₄O₂ requires: C, 86-2; H, 4-9%).

Carbonyl peak: 1675 cm⁻¹. The colour in sulphuric acid was yellow.

Peropyrene-1,10-quinone (IV). Perinaphthenone (I, 10 g) was added slowly to a hot solution of potassium hydroxide (50 g) in methanol (100 ml) and the temperature raised to 150-160° for 5 min. The melt was digested with hot water, diluted to 11. and the air bubbled through the solution for several hours. The purple precipitate was filtered off and dried (9 g). A portion was crystallized from nitrobenzene, giving a dark purple powder, m.p. above 450° (dec). (Found: C, 87°0; H, 4°0 C₂₄H₁₈O₃ requires; C, 87°6; H, 3°4%). The quinone forms a red vat with alkaline sodium dithionite solution. Absorption spectrum Fig 1. The colour in sulphuric acid was blue.

Peropyrene-1,10-quinone (IV) from the diketone (II). The diketone (II, 100 mg) was added to a solution of potassium hydroxide (10 g) in methanol (50 ml) and the temperature raised with constant stirring to $150-160^{\circ}$. The typically purple colour of the quinone (IV) developed immediately, and after dilution and oxidation with air the dark purple quinone was obtained (90 mg). The absorption

• Melting points are uncorrected and were taken in evacuated capillaries. Microanalyses by Mr. J. M. L. Cameron and his staff of this department.

¹⁹ E. Clar, W. Kelly, J. Monteath Robertson and M. G. Rossmann, J. Chem. Soc. 3878 (1956).

spectrum was identical to that shown in Fig. 1. The colour in sulphuric acid was blue. The vat with alkaline sodium dithionite was red.

Degradation of peropyrene-1,10-quinone (IV) to perylene. The solution of the quinone (IV, 1 g) in conc sulphuric acid was poured into a solution of chromium trioxide (1.4 g) in water (100 ml). This suspension was boiled for 1 hr, the solid product filtered off, extracted with dil alkali and acidified. The resulting crude acid (200 mg) was heated with soda lime under nitrogen. A little of a yellow hydrocarbon sublimed from the mixture at 380-400 $^{\circ}/0.1$ mm. The absorption spectrum of this substance in benzene was identical to that of perylene.

Peropyrene (III) from peropyrene-1,10-quinone (IV). The quinone (IV, 10 g) was ground together with zine dust (10 g) and sodium chloride (10 g). Zine chloride (50 g) was added and after the addition of water (1 ml) the mixture was melted and the temp raised with constant stirring to 290 310°, for 5 min. Digestion with dil acetic acid, removal of the zine dust with acid, and sublimation $350^{\circ}/0.02$ mm gave the golden-yellow platelets of peropyrene, (3 g). Absorption spectrum as shown in Fig. 3. The colour in sulphuric acid was blue.

Peropyrene (III) from the diketone (II). The diketone (II, 500 mg) was mixed with sodium chloride (1 g) and zinc chloride (5 g), the mixture heated with constant stirring to 300° for 5 min. After decomposition, with dil acid, the reaction product was sublimed at $350^{\circ}/0.1$ mm giving peropyrene (400 mg). When peropyrene was oxidized with selenium dioxide in nitrobenzene the resulting peropyrenequinone showed the same absorption bands as IV.

Reaction of peropyrene-1,10-quinone with maleic anhydride. The quinone (IV, 1 g) was ground with maleic anhydride (20 g) and chloranil (1 g). The mixture was heated, and the blue coloured solution turned dull red and then brown (30 min). After cooling, xylene (50 ml) was added and the crude adduct (1.4 g), filtered off. The blackish solid gave a red coloured alkaline solution which had an absorption band at 480 m μ (diffuse). The adduct was insoluble in benzene or xylene and solvents such as acetic anhydride, dimethyl formamide, trichlorobenzene etc. gave solutions on heating which showed absorption bands at 600 m μ , 555 m μ of the peropyrene quinone (IV). Dissociation to the quinone (IV) also occurred when the adduct was boiled in dil alkali (5 10%) in the presence of zinc dust. Attempts to decarboxylate the adduct by heating with soda lime gave no pure product. Heating in quinoline with copper powder gave purple solutions of the quinone (IV). The reactions described above also occurred when chloranil was omitted from the reaction mixture.

Reaction of violanthrone with maleic anhydride. When violanthrone was boiled with an excess of maleic anhydride an alkali soluble adduct was formed in good yield. The alkali solution of the adduct had an absorption band at 510 m μ . This adduct behaved in a similar way to that described above, dissociation to violanthrone occurring readily.

Phenylperopyrene. Peropyrene (500 mg) was suspended in dry benzene (100 ml) and powdered aluminium chloride (1 g) was added in portions. The mixture was heated on the water bath, the initial strong blue fluorescence changing to blood red. After decomposition in the usual manner, the yellow product (450 mg) was dissolved in xylene, and chromatographed over alumina. Fractions showing the bands at 453 m μ and 426 m μ were collected. Concentration gave yellow plattets (300 mg) of phenyl peropyrene, m.p. 310-312⁵, which sublimed at 300⁶/0⁻¹ mm. (Found: C, 95⁻², 95⁻³; H, 4⁻⁶, 4⁻⁴; C₃₃H₁₃ requires: C, 95⁻⁵; H, 4⁻⁵%). Absorption spectrum Fig. 3. The colour in sulphuric acid was blue.

Attempted cyclization of phenyl peropyrene. Phenylperopyrene (100 mg) was added to a melt of aluminium chloride (5 g) and sodium chloride (1 g) at 120°, and the temp raised to 140° for 5 min. A sample showed that the starting material bands at 453 m μ and 422 m μ were unchanged. The temp was then raised to 180–190° for 10 min, and the mixture decomposed. Sublimation at 320°/0°1 mm gave a mixture which showed a strong band at 444 m μ , that is of peropyrene, and a weaker one at 453 m μ , i.e. unchanged phenylperopyrene.

Dichloroperopyrene. This was the only product obtained from the reaction of peropyrene (III) with maleic anhydride and chloranil. Peropyrene (120 mg) was mixed with excess maleic anhydride (2 g) and chloranil (500 mg). The mixture was refluxed until the 444 m μ band of peropyrene (III) disappeared (1/2 hr) and was replaced by one at 452 m μ . Hot nitrobenzene (50 ml) was added and the dark coloured crude product filtered off and washed (112 mg). It was insoluble in alkali. Sublimation at 400⁻⁷/0⁻¹ mm, and recrystallization from trichlorobenzene gave orange red needles (5 mg) m.p. 406 409⁻⁷. (Found: C, 79⁻¹⁰, H, 3⁻¹; C₁₄H₁₃Cl₂ requires: C, 79⁻², H, 3^{-5°}₀). This

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compound gave a positive Beilstein test for chlorine. Absorption spectrum Fig. 1. The colour in cone sulphuric acid was blue.

4:4-'Dibenzanthrenyl (V). 4:4-'Dibenzanthronyl² (5 g) and zinc dust (100 g) were refluxed in pyridine (500 ml). Dil acetic acid (80 $^{\circ}_{01}$, 250 ml) was added over 4 hr and the mixture boiled for a further 4 hr. The initially pink coloured mixture was almost colourless at the end of the reduction period. The reaction product was filtered off, zinc dust destroyed with conc acid, washed with water and dil ammonia and dried (3 g). The yellowish product was crystallized from xylene under carbon dioxide. 4:4'-dibenzanthrenyl forms yellowish needles, m.p. 352-354° (dec). (Found: C, 94-3; H, 5.4 C₃₄H₂₂ requires: C, 94-8; H, 5.2°₆). Absorption spectrum Fig. 2.

Dehydrogenation of 4:4'-dibenzanthrenyl (V). When 4:4'-dibenzanthrenyl (V) was dissolved in xylene and chloranil added the solution turned yellowish green and became deep blue on boiling the mixture. The intense colour faded on cooling and a yellow compound (VI) crystallized out. The thermochromic colour change could be obtained many times before the solution lost its capacity for colourization on heating. Prolonged boiling (10-15 min) also destroyed the thermochromism, and the solution then showed the characteristically sharp bands of violanthrene (VII) at 4920, 4580, 4280 Å. Owing to its reactivity the hydrocarbon (VI) could not be obtained in analytical pure state. Dehydrogenation by heating 4:4'-dibenzanthrenyl in nitrobenzene also produced the reversible colour changes described above. When a trace of iodine was added to the nitrobenzene solution immediate conversion to violanthrene occurred.

1:2,11:12-Dibenzoperopyrene (X) and 1:2,6:7-dibenzoperopyrene (IX). Mesobenzanthrone was condensed using phosphorus oxychloride as described by Campbell and Woodham.* The product was ground up with copper powder and sublimed at 350/0-1 mm to remove any traces of halogen. The sublimate (5 g) was extracted with xylene. The first fraction was found to be 4:5,11:12-dibenzoperopyrene (VIII). Recrystallization from xylene and sublimation gave orange needles. (Found: C, 95.6; H, 4.6; calc for $C_{34}H_{18}$: C, 95.8; H, 4.2%). The absorption spectrum was identical to that described in the literature⁴ Fig. 5, m.p. 343-345°, mixed m.p. with authentic sample 343-344°. The colour in sulphuric acid was blue. The next most soluble isomer was another dibenzoperopyrene X or 1X. This was recrystallized and sublimed giving golden brown needles, m.p. 279°. The colour in conc sulphuric acid was blue. (Found: C, 95.8; H, 4.6 CatHis requires: C, 95.8; H, 4.2°). Absorption spectrum Fig. 4. A third dibenzoperopyrene IX or X was the last isomer soluble in xylene. It was recrystallized and sublimed. (Found: C, 95.8; H, 4.2. C₃₄H₁₈ requires: C, 95.8; H, $4\cdot 2\circ_0$). It crystallized from xylene in orange prisms, m.p. 334-335°. The colour in conc sulphuric acid was blue. Absorption spectrum Fig. 4. Violanthrene (VII, 1:2,9:10-dibenzoperopyrene) remained as an insoluble residue from the extraction. It was purified by repeated extraction with xylene and sublimation. The absorption spectrum and m.p. 480° confirmed the identification.

9,10-Dihydro-9,10-dihydroxy-1,4-dimethyl-9,10-di-o-toluyl anthracene (X11). o-Bromotoluene (87.5 g) was added slowly to strips of lithium metal (7 g) suspended in dry ether (250 ml) in an atmosphere of nitrogen. The reaction was started by heating the mixture gently, and the ether kept refluxing by the addition of more halide. The mixture was boiled for 2 3 hr and the ether replaced by benzene. 1,4-Dimethylanthraquinone (30 g) was added as a benzene slurry. The reaction mixture turned brick red initially and after refluxing under nitrogen (2-3 hr) became dark brown. Decomposition with ice and dil acetic acid followed by steam distillation, and extraction with alkaline sodium dithionite (3 times) to remove unreacted quinone, gave the crude diol (35 g), m.p. 234 236°. Recrystallization from benzene gave colourless needles, m.p. 244 246°. (Found: C, 86-0; H, 6-4; C₃₀H₄₂O₃ requires: C, 85-7; H, 6-7°_o). The colour in sulphuric acid was brownish red.

1,4-Dimethyl-9,10-di-0-toluyl anthracene (XIII). The diol XII (5 g) was added to a mixture of acetic acid (100 ml) and hydrogen iodide (55 %, 4 ml), and refluxed for 1 hr. The crude product (4 g) was sublimed at 180-200°/0·1 mm (3 g). Recrystallization from ethanol gave yellow needles, m.p. 170-172°. (Found: C, 93·3; H, 6·7; C₃₀H₁₀ requires: C, 93·1; H, 6·9°₀). The colour in sulphuric acid was brownish.

5:6,12:13-Dibenzoperopyrene (XIV). 1,4-Dimethyl-9,10-di-o-toluyl anthracene (XIII, 500 mg) was sublimed slowly in an air-free carbon dioxide current over lumps of 15 % palladium charcoal, held at 400°. The product from this reaction was mostly unchanged starting material. When this was removed with benzene, a purple deposit of the dibenzoperopyrene was seen which was crystallized from methylnaphthalene to give a small amount (2-3 mg) of long, thin, shining green needles. The colour and appearance of these crystals and solutions were as described in the literature, as were

the colour changes from blue to red in conc sulphuric acid. For the absorption spectrum see Fig. 6. The temp of 400° was shown to be the minimum necessary and at this temp the palladium charcoal catalyst quickly became deactivated.

3(4,11)(2-Dibenzobisanthene (XXI). 8-Chlorobenzanthrone¹¹ (4.0 g, XVI) was refluxed for 4 hr in nitrobenzene (25 ml) with copper powder (4.0 g). The crude product was filtered off and recrystallized from dimethyl formamide. The resultant 8:8'-dibenzanthronyl¹¹ (XVII, 2.0 g) was reduced at 300° in a melt of zinc dust (6.0 g), sodium chloride (6.0 g), and zinc chloride (30 g). The melt was dissolved in hydrochloric acid. After washing the product was sublimed to give a yellow hydrocarbon, which was crystallized twice from trichlorobenzene (570 mg), m.p. 432–433° and then resublimed. (Found: C, 95.6; H, 4.1; C₃₄H₁₆ requires: C, 96.2; H, 4.10°₀).

3:4,11:12-Dibenzobisanthene (XXI) dissolves slowly in conc sulphuric acid to give a violet colour. Absorption spectrum Fig. 7.

3:4,10:11-Dibenzobisanthene (XX). The eutectic mixture of 6-, and 8-chloromesobenzanthrones¹¹ (50 g XV, XVI) was refluxed with copper powder (50 g) in nitrobenzene for 4 hr. The resultant mixed dibenzanthronyls, XVII, XVIII and XIX, (5·9 g) were reduced with zinc dust (15 g) sodium chloride (15 g), and zinc chloride (75 g) at 310 for 15 min. The product was purified by sublimation and crystallization but its spectrum showed it to be a mixture. Treatment with alumimium chloride caused no alteration in the spectrum. (Found: C, 96·0; H, 4·0 C₃₄H₁₄ requires: C, 96·2; H, 4·1%). The spectrum is thus one of isomeric dibenzobisanthenes and subtraction of the 3:4,11:12-dibenzo bisanthene spectrum (Fig. 7) from that of the mixture gave a spectrum (Fig. 7) which was ascribed to 3:4,10:11-dibenzobisanthene (XX). Attempts to separate the mixture by chromatography over alumina were not successful.

Condensation of naphtho-[2':7',1:8]-anthrone (XXII). Naphthanthrone (XXII, 5-0 g) was ground up with zinc dust (15-0 g), sodium chloride (30 g) and zinc chloride (150 g). The mixture was melted and kept at 330° for 5 min, with constant stirring. The colour changed from yellow to red and then to brownish red, and traces of a red sublimate were seen. There was no frothing, since this reduction was done in the absence of water, in order to cause bimolecular condensation. The product was washed in the usual manner, and byproducts of low molecular weight were removed by extraction with petroleum ether (60–80°). The crude product was extracted with xylene in a soxhlet; since crystallization from xylene gave poor separation, the mixture (11-9 g) was chromatographed on alumina. A large amount of dinaphtho-(7':1',1:13) (1'':7'',')-peropyrene (XXIII, 3-55 g), identical with a sample prepared by Clar *et al.*¹⁰ was first obtained. After some mixed material came a pure solution which afforded reddish brown crystals of *dinaphtho* (7':1',1:13) (1":7",9:11)-*peropyrene* (XXIV, 0:4 g), m.p. 358-360°. (Found: C, 96:3; H, 3:8. C₃₁H₁₄ requires: C, 96:2; H, 3:8°,6). This compound gave a dark green colour in cone sulphuric acid. The absorption spectrum is shown in Fig. 8.

¹¹ W. Bradley and G. V. Jadhav, J. Chem. Soc. 1749 (1948); E. de Barry Barnett and M. A. Matthews, J. Chem. Soc. 2549 (1923).