

Aromatic Hydrocarbons. Part LXVI. Diperinaphthyleneanthracenes.*

By E. CLAR, W. KELLY, and (in part) J. W. WRIGHT.

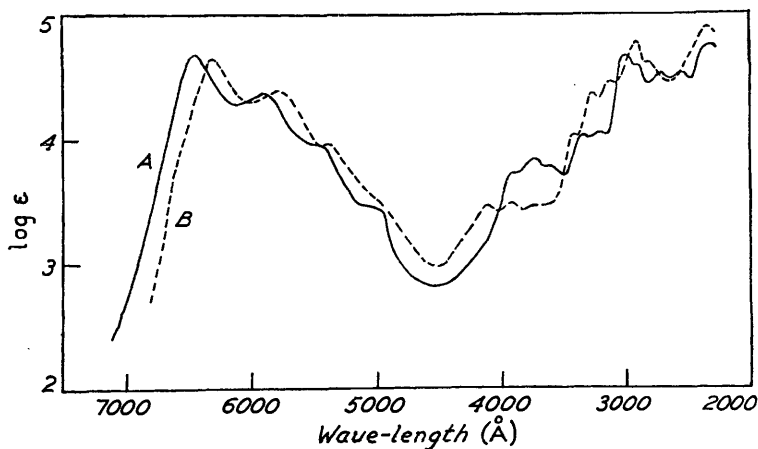
[Reprint Order No. 4737.]

1:9-5:10- and 1:9-4:10-Diperinaphthyleneanthracene have been prepared by an unambiguous method from 1:5- and 1:4-dichloroanthraquinone respectively. They show similar properties. Their absorption spectra are compared with quantum mechanical predictions by M. J. S. Dewar.

1:5- and 1:4-DICHLOROANTHRAQUINONE condense with 1-naphthylmagnesium bromide, to give the diols (I) and (IV) respectively. These are reduced by hydrogen iodide to the corresponding anthracenes, which cyclise smoothly to the hydrocarbons (II) and (V) when heated with potassium hydroxide in quinoline. For (I) ring closure in the β -position of the naphthalene radicals is excluded by the fact that the corresponding dibenzorubicene (Scholl and Meyer, *Ber.*, 1934, **67**, 1229) is completely different from (II). The structure of (II) is thus clear, and the structure (V) follows with almost equal certainty by analogy. The analogy is confirmed in that the hydrocarbons (II) and (V) show similar absorption spectra (Fig. 1). The spectra of their maleic anhydride addition products (III) and (VI) are however quite different (Fig. 2): comparison with the spectrum of benzanthrene shows the aromatic complex dominant in the spectrum of (III) to be most probably that

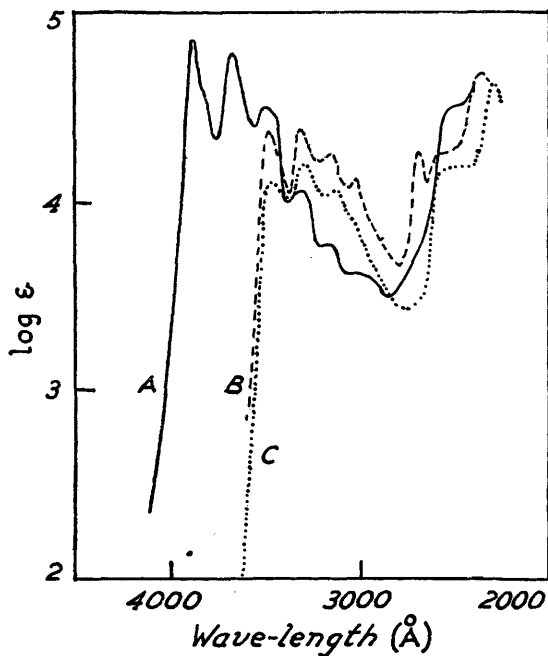
* Part LXV, *J. Amer. Chem. Soc.*, 1953, **75**, 2667.

FIG. 1.



- A, Absorption spectrum of 1 : 9-4 : 10-diperinaphthylene anthracene (V). Maxima (\AA ; $\log \epsilon$ in parentheses): 6435 (4.67), 5890 (4.36), 5440 (3.96), 5030 (3.46); 3920 (3.73), 3740 (3.84); 3360 (4.04), 3220 (4.05), 2980 (4.66) in benzene; 2720 (4.54), 2540 (4.52), 3360 (4.74) in alcohol.
- B, Absorption spectrum of 1 : 9-5 : 10-diperinaphthylene anthracene (II). Maxima: 6300 (4.64), 5790 (4.40), 5360 (3.96); 4120 (3.47), 3920 (3.47), 3720 (3.47); 3420 (4.02), 3280 (4.36), 3120 (4.44), 2920 (4.76) in benzene; 2360 (4.88) in alcohol.

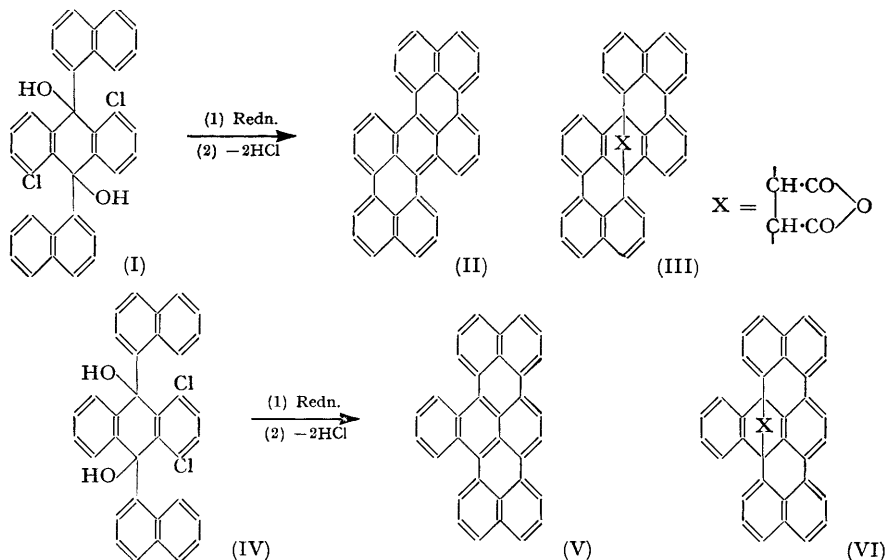
FIG. 2.



- A, Absorption spectrum of the disodium salt from the maleic anhydride adduct (III) in alcohol. Maxima (\AA ; $\log \epsilon$ in parentheses): 3880 (4.84), 3670 (4.78), 3480 (4.50), 3310 (4.06), 3160 (3.76); 2510 (4.46).
- B, Disodium salt from the maleic anhydride adduct (VI) in alcohol. Maxima: 3465 (4.37), 3290 (4.38), 3140 (4.26), 3020 (4.13); 2680 (4.23); 2380 (4.66).
- C, Benzanthrene in alcohol. Maxima: 3440 (4.14), 3290 (4.22), 3120 (4.08); 2500 (4.20); 2280 (4.64).

of benzanthrene; if an analogous addition is assumed for the addition product of V, the dibenzoterphenyl complex is the dominant feature of its spectrum.

The product (V) is identical with a hydrocarbon obtained from 9 : 10-dihydro-9 : 10-di-1'-naphthylanthracene-9 : 10-diol by an aluminium chloride ring closure. This synthesis could give (II) and/or (V). Although preference was first given to the formula (II) (Clar and Guzzi, *Ber.*, 1932, 65, 1521), later work (J. W. Wright, Thesis, Glasgow, 1949) showed that the same hydrocarbon could be obtained, by a sodium chloride-aluminium chloride melt, from 1 : 4-dichloro-9 : 10-di-1'-naphthylanthracene, and must therefore have the structure (V). The present work confirms this assignment.



The wave-lengths of the first absorption bands for (II) and (V) have been calculated by Dewar (*J.*, 1952, 3539) as 8430 and 6410 Å respectively. The observed values were 6300 and 6435 Å respectively. No other absorption band could be detected in the red as far as 10,000 Å.

EXPERIMENTAL

M. p.s were taken in evacuated capillaries. Microanalyses are by Mr. J. M. L. Cameron and Miss M. W. Christie.

1 : 5-Dichloro-9 : 10-dihydro-9 : 10-di-1'-naphthylanthracene-9 : 10-diol (I).—A suspension of finely powdered 1 : 5-dichloroanthraquinone (35 g.) in benzene (350 c.c.) was added with stirring during 15 min. to 1-naphthylmagnesium bromide prepared from 1-bromonaphthalene (103 g.) and magnesium (12 g.) in ether (200 c.c.). The temperature was allowed to rise during the addition. 200 c.c. of solvent were distilled from the mixture, which was then heated under reflux on a water-bath for 2 hr., with continuous stirring. The thick suspension was decomposed by pouring it into dilute acetic acid containing ice. Benzene and some naphthalene were removed by steam-distillation. The product was triturated and washed with ether (400 c.c.), digested thoroughly with a large excess of alkaline sodium dithionite solution to remove unchanged starting material, and washed with hot water, a pale fawn solid (38 g.) being obtained. Crystallisation from 1 : 2 : 4-trichlorobenzene gave colourless prisms, m. p. 328—329° (decomp.), of the *diol* (I) (Found: C, 76.5; H, 4.5; Cl, 13.5. $\text{C}_{34}\text{H}_{22}\text{O}_2\text{Cl}_2$ requires C, 76.6; H, 4.2; Cl, 13.3%). It gave a transient green colour changing to brown, in concentrated sulphuric acid.

1 : 5-Dichloro-9 : 10-di-1'-naphthylanthracene.—A suspension of the diol (I) (25 g.) in acetic acid (150 c.c.) and hydriodic acid (21 c.c.; 55%) was heated under reflux for 15 min., cooled, filtered, and washed with acetic acid and benzene, to give a yellow product (21 g.) which crystallised from 1 : 2 : 4-trichlorobenzene, yellow prisms, m. p. 338—339°, of 1 : 5-dichloro-

9 : 10-*di-1'-naphthylanthracene* being obtained (Found : C, 81.9; H, 4.0; Cl, 14.0. $C_{34}H_{20}Cl_2$ requires C, 81.8; H, 4.0; Cl, 14.2%). It was insoluble in concentrated sulphuric acid.

1 : 9-5 : 10-*Diperinaphthyleneanthracene* (II).—A mixture of 1 : 5-dichloro-9 : 10-*di-1'-naphthylanthracene* (2 g.), powdered potassium hydroxide (10 g.), and quinoline (12 c.c.) was heated under reflux for 45 min. The colour of the solution changed through deep red, violet-red, and bluish-violet to blue. The quinoline layer was decanted into dilute hydrochloric acid, and the deep blue precipitate, after being filtered off and washed with hydrochloric acid and water, was sublimed in vacuum at $300-310^{\circ}/8 \times 10^{-5}$ mm. Crystallisation of the sublimate (1 g.) from xylene gave deep blue prisms with a coppery sheen, m. p. $333-334^{\circ}$, of 1 : 9-5 : 10-*diperinaphthyleneanthracene* (Found : C, 95.8; H, 4.2. $C_{34}H_{18}$ requires C, 95.75; H, 4.25%). When mixed with a sample of the hydrocarbon obtained by Clar and Guzzi (*loc. cit.*), it melted at $288-296^{\circ}$. In concentrated sulphuric acid it gave a green colour which quickly became pinkish-brown. Its solution in xylene was blue with a red fluorescence.

Maleic Anhydride Adduct (III).—The hydrocarbon (II) (40 mg.) and maleic anhydride (30 mg.) were heated under reflux in xylene (20 c.c.) for 5 min.; the solution did not become colourless. During the reaction, the *adduct* crystallised as colourless prisms with a faint bluish tinge, decomp. above 200° to the blue hydrocarbon (Found : C, 87.0; H, 4.0. $C_{38}H_{20}O_3$ requires C, 87.0; H, 3.8%).

1 : 4-*Dichloro-9 : 10-dihydro-9 : 10-di-1'-naphthylanthracene-9 : 10-diol* (IV).—This preparation was similar to that of (I), but from 1 : 4-dichloroanthraquinone. Crystallisation from xylene and nitrobenzene gave colourless prisms, m. p. $312-313^{\circ}$ (decomp.), of the *diol* (IV) (Found : C, 77.4; H, 4.4. $C_{34}H_{22}O_2Cl_2$ requires C, 76.6; H, 4.2%), which dissolved in concentrated sulphuric acid to a dark greenish-brown solution.

1 : 4-*Dichloro-9 : 10-di-1'-naphthylanthracene*.—The diol (IV) was reduced as described above for the corresponding 1 : 5-dichloro-compound. The product crystallised from xylene, pale yellow needles, m. p. $341-342^{\circ}$, of 1 : 4-*dichloro-9 : 10-di-1'-naphthylanthracene* being obtained (Found : C, 81.5; H, 4.5; Cl, 13.9. $C_{34}H_{20}Cl_2$ requires C, 81.8; H, 4.0; Cl, 14.2%). It was insoluble in concentrated sulphuric acid.

1 : 9-4 : 10-*Diperinaphthyleneanthracene* (V).—(a) *By ring closure with potassium hydroxide*. The reduced 1 : 4-dichloro-compound was treated with potassium hydroxide and quinoline, as described above, though 20 min. sufficed to effect ring closure. An 83% yield of sublimed 1 : 9-4 : 10-*diperinaphthyleneanthracene* (V) was obtained. This crystallised from xylene as dark green-blue prisms or needles, m. p. $348-350^{\circ}$ (Found : C, 95.9; H, 4.3. $C_{34}H_{18}$ requires C, 95.75; H, 4.25%). There was no depression of the m. p. on admixture with Clar and Guzzi's hydrocarbon (*loc. cit.*). It dissolved in concentrated sulphuric acid to give a blue-green solution.

(b) *By ring closure with an aluminium chloride-sodium chloride melt*. The reduced 1 : 4-dichloro-compound (1 g.) was added to an aluminium chloride (5 g.)-sodium chloride (1 g.) melt at 110° . After 5 min. at $110-120^{\circ}$, the mixture was poured into dilute hydrochloric acid. The blue-black product, after being washed with hot dilute hydrochloric acid and water and dried, was chromatographed in benzene on alumina. Elution with benzene-light petroleum (b. p. $40-60^{\circ}$) gave a colourless, followed by an orange, band. A third blue-green band (benzene) yielded blue-green chlorine-containing needles, m. p. $>360^{\circ}$. A fourth, blue band on elution with benzene gave greenish-blue, glistening needles m. p. $348-350^{\circ}$, identical with the previous sample of (V).

Maleic Anhydride Adduct (VI).—The hydrocarbon (V) was heated with a large excess of maleic anhydride at $150-200^{\circ}$. Crystallisation of the product from a mixture of xylene and acetic anhydride gave colourless prisms of the adduct (VI). It was identical with Clar and Guzzi's adduct (*loc. cit.*).