637. 1,2:3,4:5,6:7,8:9,10:11,12-*Hexabenzotriphenylene.*

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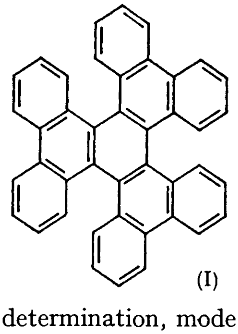
Reaction of 9,10-dichlorophenanthrene with magnesium in boiling tetrahydrofuran gives 1,2:3,4:5,6:7,8:9,10:11,12-hexabenzotriphenylene.

THE reactions of several *ortho*-dihalogenated benzenoid compounds with magnesium and lithium have recently been described:[1,2,3] it has been suggested that the polycyclic hydrocarbons produced in these reactions arise through the formation of benzyne-type intermediates. We now record a brief investigation of the reaction of 9,10-dichlorophenanthrene with these metals.


(I)

9,10-Dichlorophenanthrene was prepared by uncatalysed chlorination of phenanthrene,[4] a reaction which contrasts with the uncatalysed bromination of this hydrocarbon[5] in that only the former gives the 9,10-dihalogenated product in fair yield. 9,10-Dichlorophenanthrene was found to react only very slowly with lithium or magnesium in diethyl ether; however, it reacts with magnesium in boiling tetrahydrofuran, to give a crude neutral product from which a colourless hydrocarbon, m. p. 380°, was isolated by chromatography and fractional precipitation.

This is formulated as 1,2:3,4:5,6:7,8:9,10:11,12-hexabenzotriphenylene (I) on the basis of analysis and molecular-weight determination, mode of formation, and ultraviolet absorption (see Figure).

The ultraviolet absorption spectrum of 9,9'-biphenanthryl is described[6] as practically identical with that of phenanthrene, presumably as the result of steric prevention of

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[1] Millar and Heaney, *Quart. Rev.*, 1957, **11**, 109.

[2] Heaney, Mann, and Millar, *J.*, 1957, 3930.

[3] Hinton, Mann, and Millar, *J.*, 1958, 4704.

[4] Sandqvist and Hagelin, *Ber.*, 1918, **51**, 1515.

[5] Henstock, *J.*, 1921, **119**, 55; 1923, **123**, 3097.

[6] Henri and Bergmann, *Nature*, 1939, **143**, 278.

planarity and the resulting inhibition of conjugative interaction between the phenanthryl systems. It follows that the absorption of 9,10-di-9′-phenanthrylphenanthrene, which would give analytical values similar to those of the hydrocarbon (I), should be closely similar to that of phenanthrene, since steric inhibition of interaction between the phenanthryl systems would clearly be considerable; this compound would be expected to show $\log_{10} \varepsilon \sim 5 \cdot 3$ for the principal absorption maximum.

1,2:3,4:5,6:7,8:9,10:11,12-Hexabenzotriphenylene may be formed in this reaction by a route analogous to those postulated, for example, as possibly responsible for the formation of triphenylene in the reaction of *o*-bromoiodobenzene with lithium,[2] and of 2,6,11-trimethyltriphenylene in the reaction of 3-bromo-4-iodotoluene with lithium.[3] Such a route would involve the formation, and subsequent addition reactions, of a phenanthryne intermediate.

Ultraviolet absorption maxima (Å) *and* log ε (*in parentheses*) *of*: (*A*) 1,2:3,4:5,6:7,8:9,10:11,12-*hexabenzotriphenylene in* 1,4-*dioxan*, 2500 (5·08), 2580 (5·07), 3030 (4·35), 3520 (3·12), 3750 (2·14), 3850 (2·14); *and* (*B*) 9,10-*dichlorophenanthrene in* 95% *ethanol*, 2250 (4·45), 2570 (4·79), 2680 (4·34), 2810 4·05), 2920 (4·12), 3040 (4·18), 3280 (2·36), 3360 (2·36), 3440 (2·26).

It is noteworthy that the hydrocarbon (I) cannot be planar, as a result of steric conflict at the 1-positions of the phenanthrylene units; the deviation from planarity may be comparable with that shown by 3,4:5,6-dibenzophenanthrene, which has been examined by *X*-ray crystal analysis.[7]

Experimental

9,10-*Dichlorophenanthrene*.—Dry chlorine was passed into phenanthrene (100 g.) in carbon tetrachloride (200 ml.) at 0—5° until absorption became slow (*ca.* 80 g. during 3·5 hr.). The solvent was then removed, and the residue (which solidified at room temperature) distilled, giving the dichloro-compound, b. p. 175—185°/0·1 mm. (70—80 g., 50—60%): recrystallised from benzene, acetic acid, and ethanol, it formed colourless needles, m. p. 160·5° (lit.,[4] m. p. 160—160·5°) (Found: C, 68·1; H, 3·35. Calc. for $C_{14}H_8Cl_2$: C, 68·05; H, 3·25%). A sample oxidised with chromic anhydride and sulphuric acid in acetic acid gave 9,10-phenanthraquinone, m. p. and mixed m. p. 203°. The ultraviolet absorption spectrum of the dichlorophenanthrene is given in the Figure.

1,2:3,4:5,6:7,8:9,10:11,12-*Hexabenzotriphenylene*.—9,10-Dichlorophenanthrene (5·5 g.) in tetrahydrofuran (250 ml.) was added to magnesium (1·2 g., 2 equivs.), activated by heating with iodine or by the addition of a few drops of ethyl bromide, and the whole was stirred and boiled under reflux in a nitrogen atmosphere. After an induction period of 2—3 hr. the initially pale yellow solution became dark green as the magnesium dissolved. After being boiled under reflux for a further 2 hr., and then stirred at room temperature for 1 hr., the mixture was decanted from excess of magnesium, and the solvent was removed. Magnesium chloride was extracted from the residue by water, and the dried residue chromatographed in benzene on alumina; 9,10-dichlorophenanthrene was preferentially retained on the column. Evaporation

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[7] McIntosh, Robertson, and Vand, *J.*, 1954, 1661.

of the eluate gave the *hydrocarbon* (2·35 g., 60%), which after recrystallisation from benzene or xylene and fractional precipitation from its benzene solution by ethanol, formed a colourless powder, m. p. 380° (Found: C, 94·9; H, 5·05%. *M*, cryoscopic in phenanthrene, 558. $C_{42}H_{24}$ requires C, 95·4; H, 4·6%; *M*, 527). In a similar experiment, the mixture was carboxylated; working-up in the usual manner gave the above hydrocarbon, together with traces only of an acidic product which was not investigated.

Solutions of the hydrocarbon in benzene failed to deposit a picrate with picric acid in ethanol. The hydrocarbon was insoluble in cold concentrated sulphuric acid. In benzene or 1,4-dioxan it showed a blue fluorescence. In solid solution in 1,4-dioxan cooled in liquid nitrogen, the hydrocarbon showed a pale green phosphorescence after irradiation with high-intensity ultraviolet light.[8]

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[8] Clar, Ironside, and Zander, *J.*, 1959, 142.