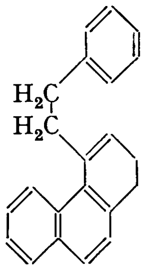
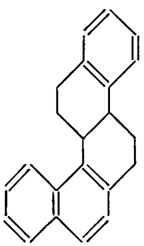
242. 1 : 2 : 5 : 6-*Dibenzphenanthrene.*

By Ernst Bergmann.

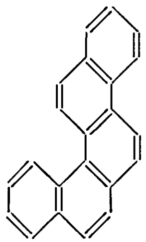
1 : 2 : 5 : 6-*Dibenzphenanthrene* (III), one of the missing pentacyclic aromatic hydrocarbons, has now been prepared, the essential step being the cyclisation of 4-β-*phenylethyl*-1 : 2-*dihydrophenanthrene* (I), which was obtained by interaction between 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene and β-phenylethylmagnesium chloride. On dehydrogenation, the oily cyclisation product yielded only partly the desired 1 : 2 : 5 : 6-dibenzphenanthrene (III) and therefore consisted only partly of the " normal " substance (II). A *hydrocarbon,* $C_{22}H_{18}$, was also obtained, for which we tentatively suggest the spiran formula (IV), which would account for the resistance to the dehydrogenating action of selenium; obviously, the hydrocarbon may also result from incomplete dehydrogenation, although in this case a substance $C_{22}H_{16}$ would be expected (leaving one hydrogenated ring). The yields were poor and a more suitable method was being sought when Prof. J. W. Cook kindly informed us that a smooth method for the synthesis of (III) has been worked out by Dr. C. L. Hewett (preceding paper). While this paper was in the press, Weidlich reported that he also had obtained 1 : 2 : 5 : 6-dibenzphenanthrene (*Ber.*, 1938, **71**, 1203).



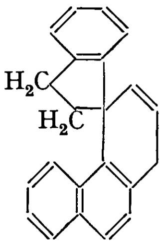
(I.)



(II.)



(III.)



(IV.)

Experimental.

4-β-*Phenylethyl*-1 : 2-*dihydrophenanthrene* (I).—4-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (Haworth, J., 1932, 1125) (12·5 g.) was added to the Grignard solution prepared from magnesium turnings (4·5 g.) and β-phenylethyl chloride (24 c.c.); to complete the reaction, it was necessary to add toluene (100 c.c.), distil off the ether, and boil the remaining mixture for 3 hours. The mass was decomposed, the solvent evaporated, and the residue heated with potassium hydrogen sulphate (15 g.) at 140° for 1 hour. The product, worked up in the usual way, was fractionated under 0·01 mm. pressure, giving a considerable head fraction, followed by the desired *compound* (I). After repeated distillation this was obtained as a yellow oil, b. p. 180°/0·01 mm., $n_D^{26^\circ}$ 1·6510 (Found : C, 92·8; H, 7·1. $C_{22}H_{20}$ requires C, 92·9; H, 7·1%).

Cyclisation. The foregoing hydrocarbon (6·5 g.) was dissolved in ice-cold carbon disulphide (65 c.c.) and, after addition of powdered aluminium chloride (13 g.), kept at 0° for 12 hours. The mass was poured into a mixture of ice and concentrated hydrochloric acid, and the product isolated by vacuum distillation as a viscous yellowish oil, b. p. 190°/0·03 mm. The analysis is satisfactory, but in view of the results of the dehydrogenation experiment reported below, the product may be non-homogeneous (Found: C, 92·5; H, 6·9. $C_{22}H_{20}$ requires C, 92·9; H, 7·1%). Yield, 4 g.

Dehydrogenation. The above cyclisation product (2 g.) was heated with selenium (4 g.) at 325—330° for 24 hours (sealed tube); charring occurred to a considerable extent. The product was isolated by means of benzene–ethyl acetate and purified by distillation in a high vacuum (0·01 mm.). The distillate solidified spontaneously and was recrystallised from glacial acetic acid. Fractionation gave (*a*) 1 : 2 : 5 : 6-*dibenzphenanthrene* (III), which formed prisms, m. p. 128°, from propyl alcohol (Found: C, 95·2; H, 5·3. $C_{22}H_{14}$ requires C, 95·0; H, 5·0%), and (*b*) a *hydrocarbon*, $C_{22}H_{18}$ (IV ?), separating from glacial acetic acid in clusters of needles, m. p. 98—100°, which sublimed easily (Found: C, 93·4; H, 6·6. $C_{22}H_{18}$ requires C, 93·6; H, 6·4%). The yield of these substances amounted to 20 mg. each. The m. p. of the former was not depressed on admixture with a specimen prepared by Dr. Hewett.

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