

THE PREPARATION OF DECACHLOROPHENANTHRENE AND DODECACHLORODIHYDROPHENANTHRENE*

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For an investigation reported elsewhere¹ it was necessary to prepare decachloro- and dodecachlorodihydrophenanthrene. Neither of these compounds is described in the literature, and in view of their possible usefulness as insecticides or fungicides the preparation and properties are given here.

Experimental

Chlorine gas was passed into a cold solution of phenanthrene (150 g) in dry carbon tetrachloride (300 ml) until much hydrogen chloride developed. When the absorption slackened, iodine (1 g) was added, and the chlorination continued at room temperature as long as the reaction proceeded briskly. The mixture was then heated slowly in an oil-bath to 60–80° and maintained at this temperature for 1 hr while the flow of chlorine was maintained. After removal of the solvent by distillation the temperature was raised to 220° and the chlorination continued for 6 hr. More iodine (0.5 g) was added and the halogenation extended for another 8 hr. The heavy brown oil resulting was poured into an evaporating basin and heated to 320° to expel hydrogen chloride. On cooling and crushing, 200 g of a brown powder was obtained.

(a) The powder (45 g) was dissolved in chlorosulphonic acid (500 ml) at 0–5° by stirring, iodine (1.5 g) was added, and the chlorination was continued in an ice-bath for 24 hr. The reaction mixture was poured onto ice and the precipitated product collected by filtration and washed with water until neutral. The dried material was heated in a porcelain dish to 250° until no more hydrogen chloride was evolved, then cooled, ground, and extracted successfully with an equal weight of carbon tetrachloride and of benzene. The residue was crystallized from boiling xylene with the addition of decolorizing charcoal. The yield was 25 g of a pale cream crystalline powder, m.p. 302°, which was raised to 306° by sublimation. The elementary analysis indicated *dodecachlorodihydrophenanthrene* (Found: C, 28.8; Cl, 71.6, 71.4. $C_{14}Cl_{12}$ requires C, 28.3; Cl, 71.7%). The isomeric identity of the dodecachloro compound was not determined.

(b) The original powder (60 g) was chlorinated as above in chlorosulphonic acid (700 ml) in the presence of iodine (1.5 g) for 30 hr. After pouring onto ice and recovery of the material by filtration, the dry product was heated in a porcelain dish to 330° until no more hydrogen chloride was evolved. The residue (45 g) was powdered, extracted with an equal weight of carbon tetrachloride, and the insoluble portion crystallized by extraction from a Soxhlet thimble with boiling xylene. The extract on cooling yielded yellow crystals (28 g), m.p. 254°. By recrystallization and sublimation the m.p. was raised to 255°. Analysis indicated *decachlorophenanthrene* (Found: C, 32.4; Cl, 67.9. $C_{14}Cl_{10}$ requires C, 32.0; Cl, 68.0%).

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¹ Brooks, J. D., Collin, P. J., Silberman, H. S., and Taylor, G. H., *Carbon*, 1966, in press.