# A 1,5-ANIONOTROPIC REARRANGEMENT IN A SUBSTITUTED 1,2-BENZANTHRACENE*

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Bergmann and Blum-Bergmann[1] have shown that 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene (I) decomposes at the melting point with the liberation of hydrogen chloride and the formation of 2-chloro-9,10-diphenylanthracene (VI). It was suggested[1] that rearrangement first gives the quinonoid intermediate (IV), that this tautomerizes to (V), which then loses hydrogen chloride to form the observed product (VI). In essence this seems to be a reasonable mechanism, especially if it is recognized that the quinonoid intermediate (IV) would be formed as a result of a 1,5-anionotropic rearrangement (I–IV).[2,3] However, the quinonoid intermediate (IV) itself would be expected to lose hydrogen chloride to give (VI) and it seems unnecessary to postulate tautomerism to the further intermediate (V).
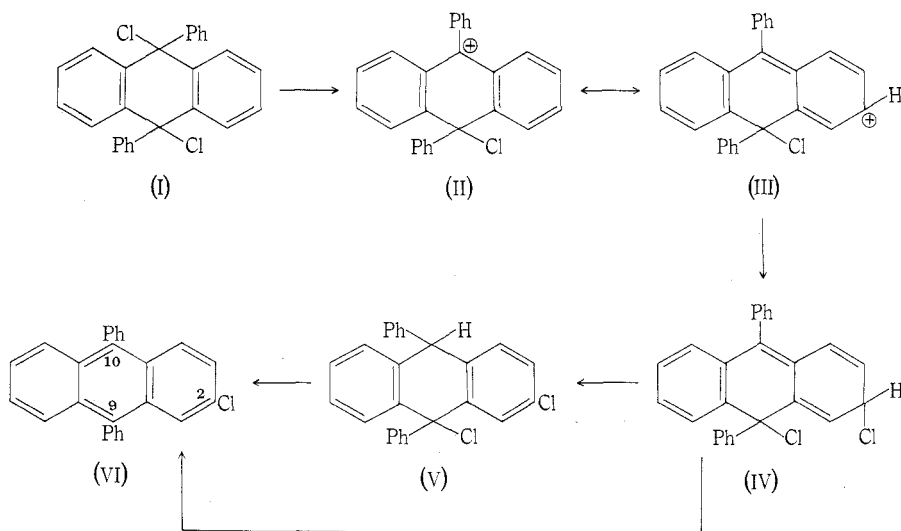
It has now been found that 9,10-dichloro-9,10-dihydro-9,10-diphenyl-1,2-benzanthracene (VII) also decomposes at the melting point, and gives a chloro-9,10-diphenyl-1,2-benzanthracene. With 1,2-benzanthracene derivatives several alternative quinonoid systems, analogous to (IV), can be drawn. However, the

[1] Bergmann, E., and Blum-Bergmann, O., *J. Amer. Chem. Soc.*, 1937, **59**, 1439.

[2] Badger, G. M., and Pearce, R. S., *J. Chem. Soc.*, 1950, 2311.

[3] Badger, G. M., and Pearce, R. S., *J. Chem. Soc.*, 1950, 2314.

known stability of 1,4-naphthaquinonoid systems relative to 1,4-benzoquinonoid structures suggested that the most probable intermediate would be (VIII), and that this would lose hydrogen chloride to give 3-chloro-9,10-diphenyl-1,2-benzanthracene (IX).

(VII)   (VIII)   (IX)
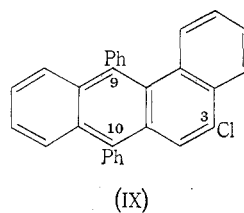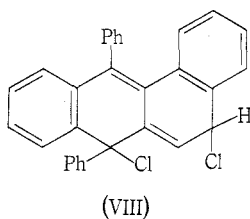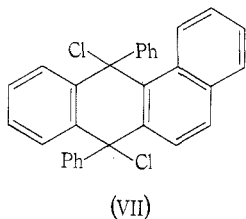
In order to confirm this hypothesis, the product was oxidized in the hope that 3-chloro-1,2-benzanthraquinone would be obtained; but the only product isolated was 1,2-dibenzoylbenzene. Accordingly, 3-chloro-1,2-benzanthraquinone[4,5] was treated with excess phenylmagnesium bromide, and the crude product reduced with potassium iodide in acetic acid to give 3-chloro-9,10-diphenyl-1,2-benzanthracene, identical with the specimen prepared as above.

Experimental

3-Chloro-1,2-benzanthraquinone

A mixture of o-(4-chloro-1-naphthoyl)benzoic acid[4] (4·0 g) and freshly distilled benzoyl chloride (8 g) was heated to 130° and concentrated sulphuric acid (0·1 ml) added slowly. Heating was continued for 1 hr and the mixture then decomposed with 6N sodium hydroxide (200 ml). The resulting product (3·0 g) was recrystallized from ethyl acetate, to give 3-chloro-1,2-benzanthraquinone as yellow needles, m.p. 181° (lit.[5] 184°).

9,10-Dichloro-9,10-dihydro-9,10-diphenyl-1,2-benzanthracene

A solution of 9,10-dihydro-9,10-diphenyl-1,2-benzanthracene[6] (5·0 g) in acetyl chloride (15 ml) was boiled under reflux. Crystalline material soon separated, and the heating was continued for 15 min. The mixture was cooled, the solid collected, washed with light petroleum (yield 4·5 g), and recrystallized from benzene/light petroleum. 9,10-Dichloro-9,10-dihydro-9,10-diphenyl-1,2-benzanthracene formed colourless prisms, m.p. c. 216–218°, depending on the rate of heating (Found: C, 80·0; H, 4·5. $C_{30}H_{20}Cl_2$ requires C, 79·8; H, 4·5%).

3-Chloro-9,10-diphenyl-1,2-benzanthracene

(i) The above dichlorodihydrodiphenylbenzanthracene (2·0 g) was heated in an oil-bath (bath temperature, 220°) until there was no further evolution of gas (30 min). The mixture was cooled, the glassy residue dissolved in a little benzene, and ethanol added. The product soon crystallized (yield 1·80 g) and was recrystallized from benzene/ethanol. 3-Chloro-9,10-diphenyl-1,2-benzanthracene formed pale yellow needles, m.p. 203–204° (Found: C, 87·1; H, 4·6. $C_{30}H_{19}Cl$ requires C, 86·9; H, 4·5%).

(ii) A solution of phenylmagnesium bromide (3·7 g) in anhydrous ether/benzene was added gradually to 3-chloro-1,2-benzanthraquinone (1·0 g) suspended in anhydrous benzene (50 ml). The mixture was cooled to moderate the exothermic reaction, then warmed on the

[4] Heller, G., Ber. dt. chem. Ges., 1912, 45, 665.

[5] Bergmann, E. D., Blum, J., and Butanaro, S., J. Org. Chem., 1961, 26, 3211.

[6] Clar, E., Ber. dt. chem. Ges., 1930, 63, 112.

steam-bath for 1 hr, cooled, and poured into ice-water (500 ml) and concentrated hydrochloric acid (10 ml). The solid was removed, the benzene layer separated, and the aqueous layer extracted with benzene. The combined benzene solutions were then exhaustively extracted with sodium hydrosulphite (to remove unreacted quinone). The benzene solution was then washed and evaporated to give a gum which could not be induced to crystallize but which was suitable for the next step. It was dissolved in glacial acetic acid (20 ml) and potassium iodide (2·0 g) added. The mixture was refluxed for 10 min, then cooled. Recrystallization of the product from benzene gave 3-chloro-9,10-diphenyl-1,2-benzanthracene, m.p. 203–204°, not depressed by admixture with a specimen prepared as above. The ultraviolet and infrared spectra of the two specimens were identical.

Oxidation of 3-Chloro-9,10-diphenyl-1,2-benzanthracene

A mixture of the above chlorodiphenylbenzanthracene (1·0 g), sodium dichromate (5 g), and acetic acid (20 ml) was refluxed for 2 hr, then poured into water. The product was collected and recrystallized from benzene/light petroleum (yield, 0·55 g). It formed colourless prisms, m.p. 146–147°, not depressed by admixture with an authentic specimen of 1,2-dibenzoylbenzene prepared by photo-oxidation of 1,3-diphenylisobenzofuran.

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne.