A New Method of Synthesizing Tetrabenzo[a, cd, j, lm]perylene and Dibenzo[cd, lm]perylene

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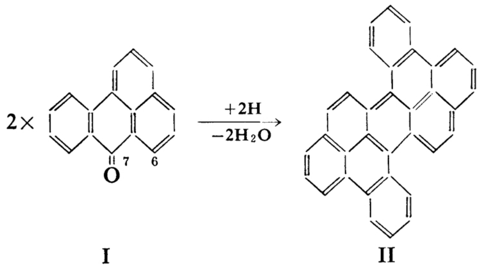
When the 6- and 7-positions of one benzanthrone (I) molecule couple with the 7- and 6-positions of another one, tetrabenzo [a, cd, j, lm] perylene (II) is formed. Similarly, by a coupling related to the carbonyl groups of two moles of benzonaphthenone (IV), dibenzo [cd, lm] perylene (V) is formed. Although the syntheses of these two hydrocarbons have already been carried out by Clar,[1,2] the procedures were quite different. Tetrabenzoperylene (II) was prepared by the condensation of two moles of benzanthrone in a benzene solution through the action of zinc dust and anhydrous aluminum chloride, while dibenzoperylene (V) was synthesized by the zinc dust fusion of benzonaphenone.

However, the present author has succeeded in the synthesis of both of them by the one following method.

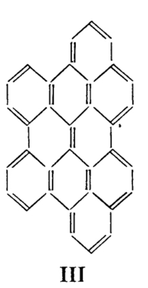
A mixture of ketone (1 part), copper powder (1 part), zinc chloride (5 parts) and sodium chloride (1 part) is kept at 220∼230°C for 30∼60 min. Then the mixture is treated with diluted hydrochloric acid, and the insoluble part collected. After the extraction of this material with chlorobenzene or *o*-dichlorobenzene, the crude product is purified by recrystallization or chromatography.

This method is not only easy to perform, but it gives rather a good yield. The author, therefore, recommends it as a general method for the condensation of such a substance.

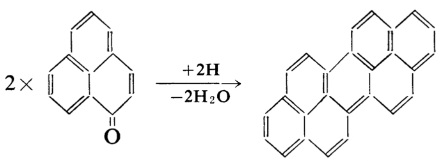


I

II



III



IV

V

Experimental

Tetrabenzo[a, cd, j, lm]perylene (II) and Dibenzo[hi, uv]bisanthene (III).—A mixture of benzanthrone (5.0 g.), copper powder (5.0 g.), zinc chloride (25 g.) and sodium chloride (5 g.) was kept at 220°C for 30 min. As the reaction proceeded, the reaction mixture became thicker and its color changed from red to black. Then the mixture was treated with warm water containing a small amount of hydrochloric acid, and the insoluble part was collected, washed and dried. Yield, 11.1 g. This product was refluxed with 100 g. of chlorobenzene for 2 hr., and the insoluble material and copper powder were removed by hot filtration. When the filtrate was concentrated, 3.95 g. of a brown crystalline powder was obtained (insoluble part, 6.65 g.). A solution of 1 g. of this product in 30 cc. of chlorobenzene was passed through a column of alumina and eluted with chlorobenzene. The first passing yellow band was separated and concentrated, giving long, fine, yellow needles (0.2 g.) which melted at 331°C (uncor.). This product was soluble in an organic solvent with a lemon yellow color and a strong grey blue fluorescence, while in a concentrated sulfuric acid solution it is blue. The absorption spectrum in benzene was identical with that of II reported by Clar.[2]

Found: C, 95.94; H, 4.34. Calcd. for $C_{34}H_{18}$·(II): C, 95.75; H, 4.25%.

On the other hand, 2.0 g. of above product (3.95 g.) was refluxed with 50 g. of benzene, and, after hot filtration, the insoluble part was sublimated in a high vaccum ($10^{-3}\sim10^{-4}$ mmHg). The orange sublimed material was collected and recrystallized from *o*-dichlorobenzene and then chlorobenzene, giving orange crystals (m. p. 305∼307°C). This substance is soluble in xylene with a greenish

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[1] E. Clar, D. R. P. 621861.

[2] E. Clar, *Chem. Ber.*, **76**, 458 (1943).

yellow color and a green yellow fluorescence, while in a concentrated sulfuric acid it is blue. Found: C, 95.95; H, 3.92. Calcd. for $C_{34}H_{16}$(III): C, 96.20; H, 3.80%. This by-product is considered to be the III reported by Clar.²⁾

Dibenzo[cd, lm]perylene (V). — A mixture of 2.0 g. of benzonaphthenone (IV), 2.0 g. of copper powder, 10 g. of zinc chloride and 2 g. of sodium chloride was kept at 220~230°C for 40 min. Then the mixture was treated with diluted hydrochloric acid, and the insoluble part was collected, washed and dried. Yield, 5.0 g. This material was refluxed with alcohol (30 ml.) for 2 hr. After the solution had cooled the insoluble part was filtered off and refluxed with xylene (50 g.) for 2 hr. The insoluble substance was then removed by hot filtration, and the filtrate was concentrated, giving 1.1 g. of a brown solid. This crude product was twice recrystallized from *o*-dichlorobenzene, giving 0.6 g. of gold yellow leaflets (m. p. 373~374°C). The sample, purified by means of chromatography on alumina with chlorobenzene, melted at 375~376°C (uncor.), and the absorption spectrum in alcohol was identical with that of V reported by Clar.²⁾ Found: C, 95.42; H, 4.53. Calcd. for $C_{26}H_{14}$(V): C, 95.68; H, 4.32%.

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