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The Condensation Products of Naphthanthrone

Shoji FUJISAWA,* Junji AOKI, Minoru TAKEKAWA, and Satoshi IWASHIMA†
Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274
†*Department of Chemistry, Faculty of Science and Technology,*
Meisei University, Hino, Tokyo 191

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Synopsis Three hydrocarbons, with absorption maximum at 510 nm, 533 nm, and 567 nm respectively, have been synthesized by the condensation of naphthanthrone in a mixed flux of zinc chloride and sodium chloride with copper powder. The structures of the hydrocarbons have been determined by comparison with the products obtained by the alkali fusion and reduction of naphthanthrone and 2-bromonaphthanthrone.

On heating naphthanthrone (6*H*-benzo[*cd*]pyren-6-one) (**1**) with copper powder in a mixed flux of zinc chloride and sodium chloride, three hydrocarbons with eleven benzene rings (**2**, **3**, **4**) have been obtained. These hydrocarbons, with overcrowed hydrogen atoms, are not only stereochemically interesting, but are also very important in the field of organic semiconductors because of their high photoconductivity.[1]

Clar *et al.* reported[2] that the fusion of **1** with zinc dust gave two hydrocarbons which had absorption maximum at 510 nm and 533 nm in benzene, respectively. The former was confirmed by X-ray analysis[3] to be diphenanthro[5,4,3-*abcd*:5′,4′,3′-*jklm*]perylene (DPP) (**2**) and the latter was tentatively assigned as dibenzoviolanthrene B (**3**) by Clar *et al.* A further hydrocarbon, with an absorption maximum at 567 nm, has been found in this laboratory and an attempt to structurally analyze this new hydrocarbon and the hydrocarbon with an absorption maximum at 533 nm has been conducted.

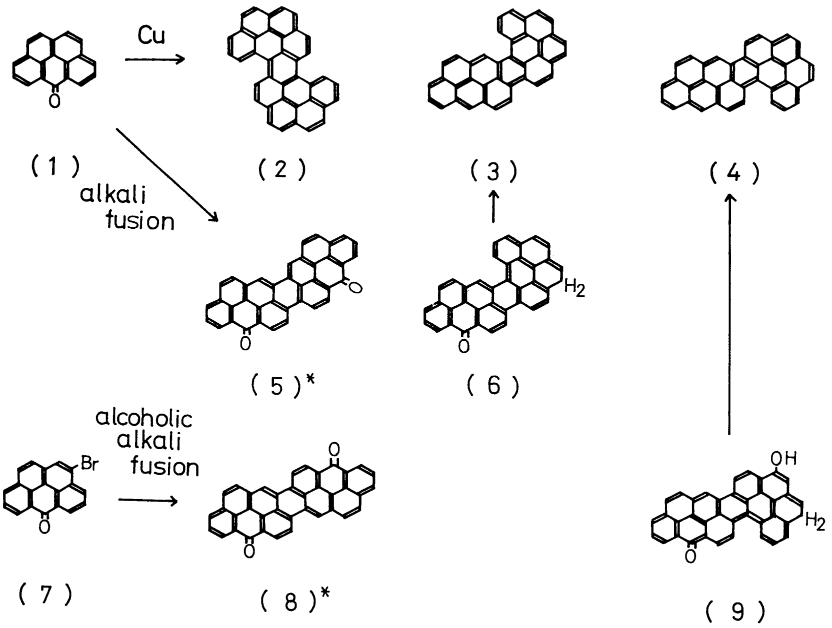
The convenient analytical methods of NMR and IR are of little use in the case of large condensed aromatic hydrocarbons because of the existence of many similar C–H bonds. Indeed the spectra are usually very complicated and consequently cannot be used as a basis for structural analysis.

X-Ray analysis is a further tool, but considerable difficulty has been met in the growing of single crystals of sufficient size. Furthermore X-ray analysis may not be easy even with good crystals.

In this paper the structures of these two hydrocarbons, deduced from the separate synthesis of each will be presented.

On the basis of the reaction used for the synthesis of violanthrones from benzanthrone,[4] the alkali fusion of **1** is expected to give dibenzoviolanthrones (**5**, **6**). Dibenzoviolanthrone B (**6**) was reduced to the corresponding hydrocarbon, dibenzoviolanthrene B (**3**), with zinc powder, melting at 378—379 °C and with an absorption maximum at 567 nm in benzene. Thus it has been concluded that dibenzoviolanthrene B (**3**) has an absorption maximum at 567 nm and not at 533 nm as suggested by Clar *et al.*[2]

On the basis of the reaction of 3-bromobenzanthrone,[4,5] the dibenzoisoviolanthrones (**8**, **9**) were prepared from 2-bromonaphthanthrone (**7**). Dibenzoisoviolanthrone B (**9**) was reduced to the corresponding hydrocarbon, dibenzoisoviolanthrene B (**4**), with zinc powder giving a hydrocarbon with an absorption max-



* (**5**, **8**). See Ref. 6.
Scheme.

imum at 533 nm in benzene. The absorption spectrum of this hydrocarbon was identical with that of one of the hydrocarbons obtained, and so it has been concluded that the hydrocarbon, with an absorption maximum at 533 nm, obtained both by authors and Clar *et al.* is dibenzoisoviolanthrene B (**4**), and not dibenzoviolanthrene B (**3**) as suggested by Clar *et al.*

Experimental

All melting points are uncorrected.

*Condensation of **1** with Copper Powder.* A mixture of **1** (2.0 g), copper powder (3.4 g), zinc chloride (17.0 g and sodium cholride (3.4 g) was kept at 270—280 °C for 1 h. The crude product was refluxed with benzene (100 ml) for 2 h and the insoluble residue, consisting mainly of copper powder, was removed by hot filtration. The filtrate on evaporation to dryness gave a dark brown solid (1.9 g). A benzene solution of this product was passed through a column of alumina and eluted with benzene. The absorbed layer was developed into three bands. The pale yellow band was separated and concentrated, giving red brown needles. Yield 0.5 g, mp 336—337 °C, $\lambda_{\max}^{\text{benzene}}$ 510 nm. The intense yellow band was the recovered naphthanthrone. The pink band, overlapping with a small amount of the brown band, was eluted with benzene, and concentrated to give a pale brown solid (mp 379—380 °C). A benzene solution of this product had an absorption maximum at 533 nm and also a small shoulder at 567 nm. The melting point and absorption spectrum were very similar to that reported by Clar *et al.* The product was dissolved in a large amount of ethanol and the solution was put into a column of alumina. The absorbed layer was developed into two bands; the lower layer, a pale brown band, was separated, concentrated and gave pale brown needles. Yield 0.25 g; mp 362 °C; $\lambda_{\max}^{\text{benzene}}$ 533 nm. The upper layer, an intense pink band, gave violet needles. Yield 0.17 g; mp 378—379 °C; $\lambda_{\max}^{\text{benzene}}$ 567 nm.

*Synthesis of **6**.* To a mixture of potassium hydroxide (10.0 g) and phenol (1.0 g) heated at 260—270 °C, naphthanthrone (1.5 g) was added. The reaction mixture was maintained at the same temperature for 1 h, and then cooled and treated with water (500 ml). The insoluble residue was collected, suspended in water (300 ml) containing sodium hydroxide (10.0 g) and heated to 60 °C. In order to remove the dibenzoviolanthrone A (**5**), ethanol (100 ml) and sodium dithionite (10.0 g) were added. Compound **5** dissolved in the sodium dithionite forming a reddish purple solution, but **6** did not, thus enabling **6** to be separated from **5**. Subsequent hot filtration separated the insoluble material (0.8 g). This product was refluxed with glacial acetic acid (100 ml) for 2 h and the insoluble material was collected by hot filtration. Yield 0.7 g. This compound corresponds to **6**.

*Reduction of **6**.* A fine powder of **6** (0.7 g) was heated with zinc dust in a mixed flux of zinc chloride (5.0 g) at 270—280 °C for 1 h. In order to remove the excess zinc dust, concentrated hydrochloric acid (25 ml) was added to the solid suspended in water (100 ml), and the insoluble material was collected. Yield 0.6 g. The crude product was refluxed with trichlorobenzene (100 ml) for 2 h and the filtrate was evaporated to dryness, giving a dark violet solid (0.5 g). A toluene solution of this substance was passed through a column of alumina, and the eluent was evaporated to give deep violet needles. Yield 0.4 g; mp 378—379 °C; $\lambda_{\max}^{\text{benzene}}$ 567 nm. Found: C, 95.65; H, 4.18%. Calcd for $C_{38}H_{18}$; C, 96.17; H, 3.83%.

*Synthesis of Dibenzoisoviolanthrone B (**9**).* A mixture of potassium hydroxide (10.0 g), phenol (2.0 g) and isopropyl alcohol (7.0 g) was heated at 170—180 °C. 2-Bromonaphthanthrone (**7**) (1.0 g) was added and the mixture was stirred for 4 h at the same temperature. The reaction mixture turned green immediately, then dark olive green, and finally blue green. The mixture was poured into water (100 ml) and oxidized by air. The precipitate was collected and suspended in water (200 ml) containing sodium hydroxide (10.0 g), ethanol (100 ml) and sodium dithionite (10.0 g), and maintained at 55—60 °C for 15 min. Compound **9** was collected by the same procedure used for the separation of **6** from **5** using sodium dithionite. After hot filtration, the insoluble material was collected. Yield 0.6 g. The product was boiled in glacial acetic acid (50 ml), cooled and the insoluble material was filtered. Yield 0.55 g. This product is assumed to be **9**.

*Reduction of **9**.* A fine powder of **9** (0.5 g) was treated with zinc dust (0.5 g) in a mixed flux of zinc chloride and sodium chloride at 270—280 °C for 1 h. The precipitate was filtered and dried. In order to remove the zinc dust, the precipitate was refluxed with toluene (100 ml) for 2 h and, after hot filtration, the filtrate was evaporated to dryness, giving a dark brown solid (0.4 g). Further purification was conducted by column chromatography of alumina with toluene.

The eluent was evaporated to dryness and gave pale brown needles. Yield 0.1 g; mp 362 °C; $\lambda_{\max}^{\text{benzene}}$ 533 nm. Found: C, 95.85; H, 4.18%. Calcd for $C_{38}H_{18}$. C, 96.17; H, 3.83%.

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