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The Thermal Treatment of Dibenzanthronyls

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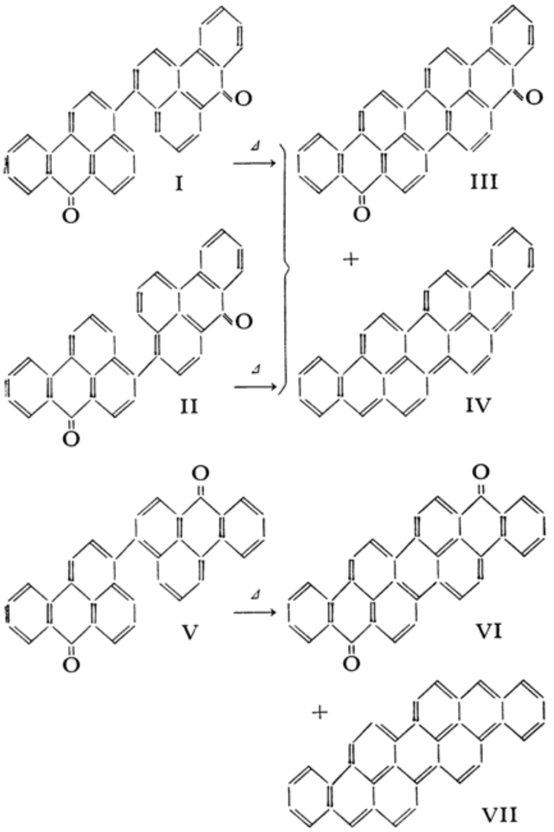
The ring closure of 3, 3′-dibenzanthronyl to form dibenzanthrone was previously effected by means of homogeneous melting at 430°C in an open vessel or in vacuo (Y. Nagai et al., *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **67**, 1977 (1964)). In this report, the thermal treatment of 3, 3′-dibenzanthronyl and its isomers, 3, 4′- and 4, 4′-dibenzanthronyls, in a closed vessel is described. The reaction was carried out in the following way: a glass tube was filled with finely-powdered dibenzanthronyl. The tube was then placed in a stainless-steel bomb and heated to 425—435°C for 25 min. Thus, 3, 3′- or 4, 4′-dibenzanthronyl yielded dibenzanthrone and dibenzanthrene, along with a putative secondary thermal reaction product in the form of a black powder; the nature of this briefly discussed. Similarly, 3, 4′-dibenzanthronyl was converted to isodibenzanthrone and isodibenzanthrene, together with a black powder.

Upon being heated in a closed vessel at 425—435°C, 3, 3′-dibenzanthronyl (I) or 4, 4′-dibenzanthronyl (II) was converted into dibenzanthrone (violanthrone) (III) and dibenzanthrene (IV). Similarly, 3, 4′-dibenzanthronyl (V) was turned into isodibenzanthrone (isoviolanthrone) (IV) and isodibenzanthrene (VII) by the same thermal treatment.



Previously 3, 3′-dibenzanthronyl (m. p. 430°C, uncorr.) was found to suffer from ring closure and to give dibenzanthrone when melted at 430°C in an open vessel under ordinary atmospheric pressure or in vacuo.1) Its isomers, 3, 4′-dibenzanthronyl (m. p. 330—331°C, uncorr.) and 4, 4′-dibenzanthronyl (m. p. 338—339°C, uncorr.), were, however, not changed by the same treatment, for sublimation prevailed under these conditions. On the other hand, the interference values between hydrogen atoms at the 3- and 4-positions of the benzanthrone residues of these dibenzanthronyls were supposed to be of approximately the same magnitude, and no considerable topochemically-significant differences were found among them. Therefore, further investigations have been made as to whether these dibenzanthronyls give the quinones upon thermal treatment in a vessel closed so as to prevent sublimation. It was thus found, that on separating the pyrolyzed product, the threne was formed unexpectedly, along with the quinone, as has been mentioned above. In addition, when the dibenzanthronyl was heated above 425°C in a closed vessel, a "secondary" thermal reaction product was also obtained as a black powder which dissolved in concentrated sulfuric acid, giving a dark blue color at 50°C. It showed a single, sharp absorption of electron spin resonance, with a spin concentration of the order of 10^{20} spin/g. in the case of 3, 3′-dibenzanthronyl. The shape of the absorption curve indicated that the by-product was not a mere amorphous, graphite-like matter resulting from carbonization. Although further studies of its nature have yet to be carried out, a tentative structure is give in VIII, taking into consideration the fact that the partial reduction product of the quinone, such as that shown in IX, was not separated.

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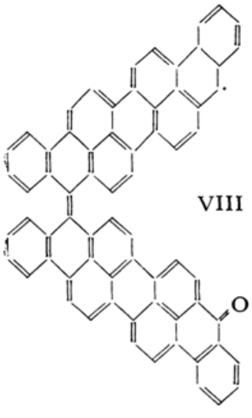
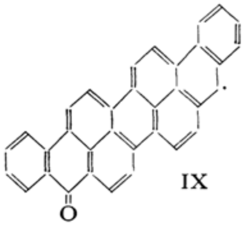
1) Y. Nagai and K. Nagasawa, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **67**, 1977 (1964).



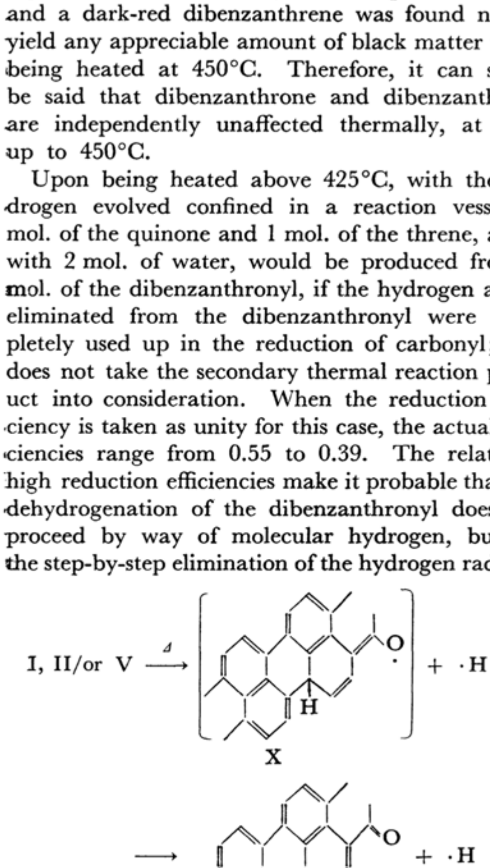
VIII



IX

In this connection, dibenzanthrone itself has been reported to be thermally stable up to 475°C,[2] and a dark-red dibenzanthrene was found not to yield any appreciable amount of black matter upon being heated at 450°C. Therefore, it can safely be said that dibenzanthrone and dibenzanthrene are independently unaffected thermally, at least up to 450°C.

Upon being heated above 425°C, with the hydrogen evolved confined in a reaction vessel, 2 mol. of the quinone and 1 mol. of the threne, along with 2 mol. of water, would be produced from 3 mol. of the dibenzanthronyl, if the hydrogen atoms eliminated from the dibenzanthronyl were completely used up in the reduction of carbonyl; this does not take the secondary thermal reaction product into consideration. When the reduction efficiency is taken as unity for this case, the actual efficiencies range from 0.55 to 0.39. The relatively high reduction efficiencies make it probable that the dehydrogenation of the dibenzanthronyl does not proceed by way of molecular hydrogen, but by the step-by-step elimination of the hydrogen radical:



X

This assumption makes it necessary to consider a radical, such as that shown in X, as a presumed transient intermediate for the threne and the secondary thermal reaction product.

The analogous ring closure by means of the thermal treatment of a polynuclear aromatic compound which possesses sterically-hindered C–H bonds is rather sporadic, according to the literature. To cite an example, Clar et al.[3] reported that tetrabenzoperopyrene melts at 482°C, with the evolution of hydrogen, and that it resolidifies with the formation of hexabenzocoronene; the latter can also be obtained from less densely-fused hexaphenylbenzene.[4]

Experimental

The Preparation of Dibenzanthronyls.—*3, 3′-Dibenzanthronyl.*—3, 3′-Dibenzanthronyl was prepared by the condensation of benzanthrone with manganese dioxide in a concentrated sulfuric acid - polyphosphoric acid medium.[5] Purified 3, 3′-dibenzanthronyl, which was negative in its ESR spectum, had a m. p. of 430°C (uncorr.) and was in the form of microscopic yellow needle crystals.

3, 4′-Dibenzanthronyl (II).—3, 4′-Dibenzanthronyl was prepared by cross condensation between 3-chlorobenzanthrone and benzanthrone in sodium anilide at 0°C, following the method of Luttringhaus et al.[6] Purification was carried out with chromatography*1 and recrystallization (m. p. 330—331°C, uncorr.) (331—332°C in the literature), resulting in yellow needle crystals. For the sake of identification, these crystals were then melted with potassium hydroxide; the infrared spectrum of the resultant black violet powder coincided with that of an authentic specimen of isodibenzanthrone.

4, 4′-Dibenzanthronyl.—4, 4′-Dibenzanthronyl was prepared by the alcoholic potash-fusion of benzanthrone at 105°C.[7] With recrystallizations, followed by chromatographic purification, 4, 4′-dibenzanthronyl was obtained as pale yellow plate et crystals (m. p. 338—339°C, uncorr.) (326°C, corr., in the literature). After being subjected to kali-fusion, the resultant black violtet powder was identified from its infrared spectrum as dibenzanthrone.

The Thermal Treatment of Dibenzanthronyls.—*3, 3′-Dibenzanthronyl.* — Finely-powdered 500 mg. of 3, 3′-dibenzanthronyl were charged into a semi-hard glass tube, the open side of which was pulled to a capillary and bent downward. When the tip of the capillary was closed, the glass tube exploded at an elevated temperature in a reaction tube, necessitating the troublesome separation of the glass pieces scattered in the organic matter. The tube was then placed in a stainless-steel reaction tube with a needle bulb mounted on it, and the whole was installed in an electric furnace which had previously been heated to 300°C. Then the temperature was rapidly raised

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2) G. Gibson, M. Holohan and H. Riley, *J. Chem. Soc.*, **1946**, 456.

3) E. Clar, C. T. Ironside and M. Zander, ibid., **1959**, 142.

4) A. Halleux, R. H. Martin and G. S. D. King, *Helv. Chim. Acta*, **41**, 1177 (1958).

5) Y. Nagai and K. Nagasawa, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **68**, 1906 (1965).

6) A. Lüttringhaus and H. Nereshimer, *Ann.*, **473**, 259 (1929).

*1 Commercial alumina for chromatography was deactivated hygroscopically, so that the R_f value (the ratio of development in the radial direction) of the benzanthrone dissolved and developed with benzene lay between 0.6 and 0.7 in disk chromatography. The deactivated alumina is used throughout this report whenever the utilization of alumina or chromatography is described.

7) T. Maki, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **46**, 1256 (1943).

to 450°C (inner temperature; 430±5°C) (the pressure gauge indicated 2.5 kg./cm^2 at the maximum). After being kept for 25 min. at that temperature, the reaction tube was immediately taken out of the furnace and cooled to room temperature. By cutting the glass-tube, a dull black-violet mass was obtained. This was pulverized and extracted by refluxing it with 100 g. of *o*-dichlorobenzene. Extraction was repeated as long as a green fluorescence remained in the filtrate. The extracts were then condensed and passed through 5 g. of an alumina layer on a glassfilter (1.5 cm. in diameter). The alumina layer was successively washed with hot *o*-dichlorobenzene until no green fluorescence could be observed in the eluate. *o*-Dichlorobenzene solutions were collected and condensed, then subjected to steam distillation to yield 110 mg. of a dull brownish-red powder, which dissolved in concentrated sulfuric acid with a bluish-green color. After this powder had been sublimed in vacuo, 75 mg. of a dark red crystalline powder were obtained. It did not melt at 450°C, and its infrared spectrum was identical with that of an authentic specimen*2 at the following absorption maxima in the fingerprint region; 735, 742, 784, 818, 840, 870, 938, 1015, and 1198 cm^{-1} (NaCl prism, KBr tablet).

The alumina layer, now free from the reduction product, was impregnated with black violet quinone and the secondary thermal reaction product. It was treated with concentrated sulfuric acid at 50°C, and then the acid was filtered off. The violet filtrate was poured into ice water, and a dark-colored precipitate was collected and washed with water. Then, in the form of a dull black slurry, the material was treated with an alkaline sodium dithionite solution at 50—60°C. A red-violet vat was filtered and washed with a warm alkaline sodium dithionite solution to which a small quantity of ethyl alcohol had been added. The vat was then triturated by aeration at room temperature. A black violte precipitate was collected by filtration and dried at 110°C to give 215 mg. of dibenzanthrone (43.4% of the theoretical yield, based on 3, 3′-dibenzanthronyl). This gave a red-fluorescent blue solution with hot *o*-dichlorobenzene and dissolved in concentrated sulfuric acid with a reddish-violet color. Coincidences between its infrared spectrum and that of an authentic specimen were observed at the following absorption maxima; 694, 753, 807, 951, 1034, 1195, 1281, 1298, 1336, 1381, 1450, 1572, and 1642 cm^{-1}.

Unvattable black powder was thoroughly washed with water and dried at 110°C, and then refluxed with 30 g. of nitrobenzene for 1 hr. and filtered while hot. The refluxing was repeated as long as a red fluorescence persisted in the filtrate. Thus, 85 mg. of black powder which was practically insoluble in nitrobenzene were obtained. It became dark blue in warm concentrated sulfuric acid, and when boiled with *asym*-trichlorobenzene, a small quantity of it dissolved and became dark blue. It gave rise to a very sharp ESR signal, corresponding to about 10^{20} spin/g., and showed absorption maxima at $\lambda_{max}^{\text{conc.}H_2SO_4}=720$ and 580 mμ. Its infrared spectrum showed an ill-defined absorption at about 1640 cm^{-1}.

When the thermal treatment of 3, 3′-dibenzanthronyl was carried out in a sealed tube at 470°C, no dibenzanthrone was separated, but 70 mg. of dibenzanthrene and 305 mg. of the secondary thermal reaction product were obtained from 500 mg. of the sample.

4, 4′-Dibenzanthronyl.—Under the same conditions as in the case of 3, 3′-dibenzanthronyl, a 100 mg. portion of finely-powdered 4, 4′-dibenzanthronyl was submitted to heating in a sealed tube at 425—435°C for 25 min., yielding 94 mg. of a black powder with a greenish hue. The black powder was then dissolved in 40 cc. of concentrated sulfuric acid at 50°C and poured into ice water. The precipitates were collected and washed until they were neutral. The greenish-black slurry was treated with 50 cc. of a warm alkaline sodium dithionite solution to which 3—4 cc. of pyridine had been added. By filtering and air-oxidizing the red-violet vat, 21 mg. of dibenzanthrone were obtained (21.2% of the theoretical yield). After the unvattable portion had been washed thoroughly with water and then dried, it was refluxed with 50 cc. of nitrobenzene for a few hours. The solution was then passed through 1 g. of alumina on a glass-filter. The eluate was condensed and steam-distilled to give 19 mg. of crude dibenzanthrene, which were recrystallized from *asym*-trichlorobenzene to yield 13 mg. of dibenzanthrene. From the alumina layer, 30 mg. of the secondary thermal reaction product were obtained as a black powder. The infrared spectra of dibenzanthrone and dibenzanthrene were identical with those of the authentic specimens.

3, 4′-Dibenzanthronyl. — Finely-powdered 100 mg. of 3, 4′-dibenzanthronyl were treated at 425—435°C for 25 min. in a sealed tube. The resultant 93 mg. black mass was treated much as in the case of 4, 4′-dibenzanthronyl. From a clear bluish-violet vat, 38 mg. of isodibenzanthrone (38.4% of the theoretical yield) were obtained. This dissolved in concentrated sulfuric acid with a green color, and its infrared spectrum coincided at the following absorption maxima with that of an authentic specimen; 702, 750, 805, 977, 1077, 1281, 1310, 1380, 1474, 1501, 1563, 1588, and 1638 cm^{-1}.

Out of the unvattable portion, 30 mg. of crude isodibenzanthrene were separated; after this had been sublimed in vacuo, 12 mg. of isodibenzanthrene were obtained as a dark red crystalline powder which did not melt at 450°C. Coincidences of the infrared spectrum with that of an authentic specimen at the following maxima in the fingerprint region were observed; 737, 745, 790, 826, 876, 934, 1020, and 1186 cm^{-1}.

Besides the above reaction products, 13 mg. of a black powder were yielded; this powder dissolved in concentrated sulfuric acid at 70°C with a dark color.

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*2 The authentic specimens of dibenzanthrene and isodibenzanthrene were prepared by means of the Clar reduction of pure dibenzanthrone and isodibenzanthrone respectively, followed by purification with sublimation in vacuo (E. Clar, *Ber.*, **72**, 1645 (1939); J. Aoki, dissertation, The University of Tokyo, 1964).