Studies of Violanthrone B. I. Reduction and Oxidation of Violanthrone B[1]

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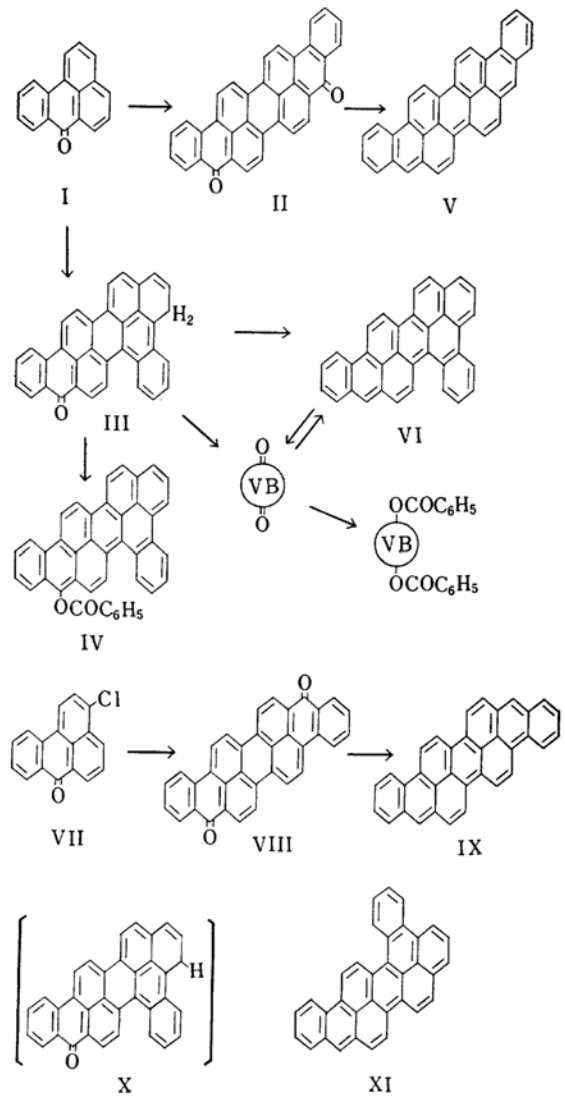
When benzanthrone (I) is fused with potassium hydroxide in the presence of phenol or sodium acetate, by its own condensation, violanthrone (II) is obtained; this substance is very useful as a vat dye. On the other hand, as a by-product, a black violet compound which is worthless as vat dye is obtained; this compound is barely vattable at 65~70°C. This worthless compound was found by the study of Maki and denoted as violanthrone B[2]. Further, he suggested III as its formula with one carbonyl group. Although this assumption has been partially confirmed by studies on the condensations of benzanthrone derivatives by Maki and Nagai[3], there remain many doubtful points. Furthermore, recently it has been found by Akamatu and Maekawa[4] that this substance was paramagnetic and that it may be a new radical compound to be known as formula X. Their studies are quite interesting and valuable in the field of the chemistry of this polynuclear system.

From the result of elementary analysis and the preparation of the leucobenzoate (IV) which was obtained by the author by the addition of benzoyl chloride to the vat solution, it has been found, however, that this substance has only one carbonyl group. Following the reduction technique of Clar[5], in which violanthrone A[6] was reduced to violanthrene A (V) with zinc dust in the mixed flux of zinc chloride and sodium chloride, the author obtained the reduction product from violanthrone B. This compound resembles violanthrene A, which shows a strong yellow green fluorescence in organic solvent and is green when dissolved in concentrated sulfuric acid. It is, however, evident that this substance is apparently different from violanthrene A; the reduced compound is more soluble than violanthrene A in organic solvent and the melting point of the former is 344°C (corr.), while that of the later is higher than 360°C[5,7]. In addition, this compound is not identical with isoviolanthrene (IX)[5] either, the reduction product of isoviolanthrone (VIII) prepared by



1) Read befroe the 13th Annual Meeting of the Chemical Society of Japan, April, 1960.

2) T. Maki, *J. Chem. Soc. Ind., Japan* (*Kôgyô Kwagaka Zasshi*), 35, 1441 (1932); *Chem. Abstr.*, 27, 1629 (1933).

3) T. Maki, ibid., 38, 1390 (1935); *Chem. Abstr.*, 30, 2008 (1936); T. Maki and A. Kikuchi, ibid., 43, 763 (1940); *Chem. Abstr.*, 35, 1783 (1941); Y. Nagai et al., ibid., 47, 529 (1944).

4) H. Akamatu and T. Maekawa, Presented at the 13th Annual Meeting of the Chemical Society of Japan, April, 1960.

5) E. Clar, *Ber.*, 72, 1648 (1939).

6) "A" is used to distinguish it from the B-compound.

7) E. Clar, *Ber.*, 76, 458 (1943).

the bimolecular self condensation of 3-chlorobenzanthrone (VII), because isoviolanthrene is yellow green rather than green when dissolved in concentrated sulfuric acid and melts at a temperature higher than 360°C[5,7]. From the results of his chemical analysis, the author has concluded that the reduction product is a new hydrocarbon having a "dibenzanthrene" type skeleton. We denote this hydrocarbon violanthrene B (VI).

When violanthrene A was oxidized with dilute sulfuric acid and potassium bichromate, the author obtained violanthrone A. In an effort to obtain violanthrone B, violanthrene B (VI) was oxidized, but violanthrone B (III) was not obtained. The oxidized product is readily vattable at 30°C and cotton is dyed in it a dark violet. The result of elementary analysis suggested that it may be a quinone of a dibenzanthrene type. This assumption was confirmed by the author, who synthesized its leucodibenzoate at m. p. 335~336°C (corr.).

However, he has found the more interesting fact that the quinone can also be prepared from violanthrone B (III) by a similar operation. Further, from this quinone violanthrene B (VI) was obtained again by zinc dust fusion.

In conclusion, it is reasonable to suppose that all derivatives from violanthrone B have the same polynuclear skeleton, but not those of violanthrene A and isoviolanthrene A.

On the other hand, it has been confirmed by the author that violanthrone B has only one carbonyl group, and further, it has been reported by Nagai et al. that the 6-position of benzanthrone contributes to the formation of the B-compound[3]. Consequently, the hypothetic skeleton (IV), submitted by Maki, coincides with the above facts, but the isomeric formula XI must also be re-considered for the same reason. A detailed discussion will be presented in a later report.

Experimental

Violanthrone A (II) and Violanthrone B (III).—These substances were prepared by the operation stated in Maki's paper[2], but for the purpose of increasing the yield of B-compound, the condition of the alkali fusion was somewhat modified as below. Benzanthrone (I) (10.0 g.) was fused with 40 g. of 85% potassium hydroxide and 4.2 g. of phenol at 220°C for 30 min. (Ref. 2 : 81% potassium hydroxide, 12.4 g. of phenol, 1 hr.).

Violanthrone A was obtained as one product, vattable at 55°C and insoluble in chlorobenzene. Yield, 2.5 g. of violet black powder. The concentrated sulfuric acid solution shows a pure violet color.

The other product, which was barely vattable and insoluble in glacial acetic acid, was violanthrone B. Yield, 5.4 g. of violet black powder. It is soluble in concentrated sulfuric acid as a blue color[8].

Found: C, 91.47; H, 4.35. Calcd. for $C_{34}H_{18}O$ (III): C, 92.28; H, 4.10%.

Leucobenzoate of Violanthrone B (IV).—Violanthrone B (III) (0.50 g.) was vatted by heating with 10 g. of sodium hydroxide, 10 g. of sodium hydrosulfite and 200 ml. of water at 70°C and 5 g. of benzoyl chloride was added. The mtxture was shaked without heating for 2 hr. After being allowed to stand overnight, the precipitate was collected and washed neutral. Yield, 0.50 g. of dark brown powder. The product was recrystallized from xylene-petroleum ether, giving red brown needles, m. p. 327~328°C (uncorr.), 340~341°C (corr.). The product is soluble in organic solvent with a strong yellow green fluorescence and in concentrated sulfuric acid solution shows at first a blue color and then a blue green.

Found: C, 89.92; H, 4.19. Calcd. for $C_{41}H_{22}O_2$ (IV): C, 90.09; H, 4.06%.

Violanthrene B (VI).—Two gram of violanthrone B (III) in the form of fine powder, was kept with 2.0 g. of zinc dust in the mixed flux of 10 g. of zinc chloride and 2.0 g. of sodium chloride at 260°C for 20 min. Then the mixture was treated with 300 ml. of water and the insoluble material was filtered off. To remove the excess of zinc dust, it was suspended in 100 ml. of water and 30 ml. of concentrated hydrochloric acid was added. After being kept overnight, the insoluble was collected and washed neutral. The crude reduction product (1.8 g.) was sublimated in a high vaccum (10^{-3}~10^{-4} mmHg) and recrystallized from 100 parts of *o*-dichlorobenzene, giving orange red needles, m. p. 328°C (uncorr.), 341°C (corr.). This product is soluble in organic solvent with a strong yellow green fluorescence, and in the concentrated sulfuric acid solution shows at first blue and then green, after which it changes no more.

Found: C, 95.56; H, 4.32. Calcd. for $C_{34}H_{18}$ (VI): C, 95.75; H, 4.25%.

Violanthrene A (V).—Synthesis was carried out by a method similar to that used for VI[9]. The crude product (1.8 g.) obtained from 2.0 g. of violanthrone A (II), was sublimated in high vaccum and refluxed with 100 g. of *o*-dichlorobenzene for 30 min. The small amount of soluble impurities was removed by hot filtration. Yield, 0.6 g. of brown red crystalline powder, m. p. 476~478°C (uncorr.)[10]. This substance is only with difficulty soluble in organic solvent and in a concentrated sulfuric acid solution shows green color.

Isoviolanthrene A (IX).—Synthesis was carried out by a method similar to that used for V. Yield, 32% from isoviolanthrone (VIII). Dark red crystalline powder, m. p. 506~508°C (uncorr.)[11]. The product is only with difficulty soluble in organic solvent and appears as a yellow green coloration in concentrated sulfuric acid.

Oxidation of Violanthrene B.—To a solution of

8) The sample was purified by means of chromatography on anhydrous sodium carbonate from *o*-dichlorobenzene.
9) Cf. also Ref. 5
10) Ref. 7, m. p. 478°C.
11) Ref. 7, m. p. 510°C.

1.00 g. of violanthrene B (VI) in 30 ml. of concentrated sulfuric acid was added, with cooling, 30 ml. of water. After cooling till the room temperature, 1.0 g. of potassium bichromate, which had been dissolved in 20 ml. of water, was added. The mixture was stirred for 3 hr. on a boiling water bath and, after being diluted with 300 ml. of water, was filtered. The unchanged VI was separated as the insoluble part by treating it with a 2% alkaline hydrosulfite solution at 30°C, and 0.95 g. of the oxidation product was obtained from the violet filtrate by air oxidation. The crude product, finely powdered, was boiled with 300 g. of *o*-dichlorobenzene with reflux for 2 hr., and insoluble impurities was removed by hot filtration. The filtrate was evaporated to a volume of about 100 ml. for crystallization. The crystal (0.65 g.) formed was recrystallized from chlorobenzene, giving black violet needles, melting point higher than 360°C. The product shows pure blue when dissolved in concentrated sulfuric acid and reddish violet in a hot organic solvent, but it is readily vattable at 30°C while III is with difficulty vatted even at 60°C.

Found: C, 88.74; H, 3.83. Calcd. for $C_{34}H_{16}O_2$; C, 89.46; H, 3.53%.

Leucodibenzoate. — The oxidation product (0.50 g.) was vatted by heating with 8 g. of sodium hydroxide, 10 g. of sodium hydrosulfite and 200 ml. of water at 50°C and 5.0 g. of benzoyl chloride was added. The mixture was shaked without heating for 2 hr. and allowed to stand overnight. The precipitate was then collected and the unchanged substance was removed by treating with an alkaline hydrosulfite solution as the insoluble part. The crude product (0.45 g.) was recrystallized repeatedly from *o*-dichlorobenzene-petroleum ether, giving orange brown needles, m. p. 322~323°C (uncorr.), 335~336°C (corr.). This product is only with difficulty soluble in alcohol, when dissolved in benzene, xylene and *o*-dichlorobenzene gives a strong yellow green fluorescence, and in a concentrated sulfuric acid solution gives a bluish green coloration.

Found: C, 85.96; H, 3.93. Calcd. for $C_{48}H_{26}O_4$: C, 86.47; H, 3.93%.

Oxidation of Violanthrone B.—By an operation similar to that used for VI, 2.00 g. of violanthrone B (III) was oxidized with 2.0 g. of potassium bichromate and diluted sulfuric acid, and 1.65 g. of crude product was obtained from an alkaline hydrosulfite vat as the soluble part (the insoluble, 0.30 g.). It was boiled with 300 g. of *o*-dichlorobenzene, and 1.00 g. of violet black needles of a melting point higher than 360°C were obtained from the filtrate after hot filtration. The product was easily vattable, was soluble in concentrated sulfuric acid, appearing as a pure blue color, and its absorption spectrum and leucobenzoate are identical with those of the oxidation product of violanthrene B.

Reduction. — By zinc dust fusion 0.20 g. of the above mentioned quinone was reduced. The crude product was purified by sublimation in high vacuum and recrystallization from *o*-dichlorobenzene. Yield, 0.06 g. of orange red needles, m. p. 326~328°C (uncorr.). This product was identical with violanthrene B (VI).

Oxidation of Violanthrene A.—By an operation similar to that used for VI, 1.00 g. of violanthrene A was oxidized with 1.0 g. of potassium bichromate and diluted sulfuric acid. The crude product was treated with 3% alkaline hydrosulfite solution at 60°C, and the unchanged substance was removed as the insoluble. From the red violet filtrate, 0.85 g. of the oxidation product was obtained. It was boiled with 100 g. of chlorobenzene for 1 hr., filtered and dried. Yield, 0.80 g. of violet black powder, melting point higher than 360°C. The product was soluble in concentrated sulfuric acid, giving a pure violet color, and, further, any other properties were also identical with those of violanthrone A (II) (Found: C, 89.11; H, 4.03%).

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