Studies of Violanthrone B. II. Reduction of Isoviolanthrone B

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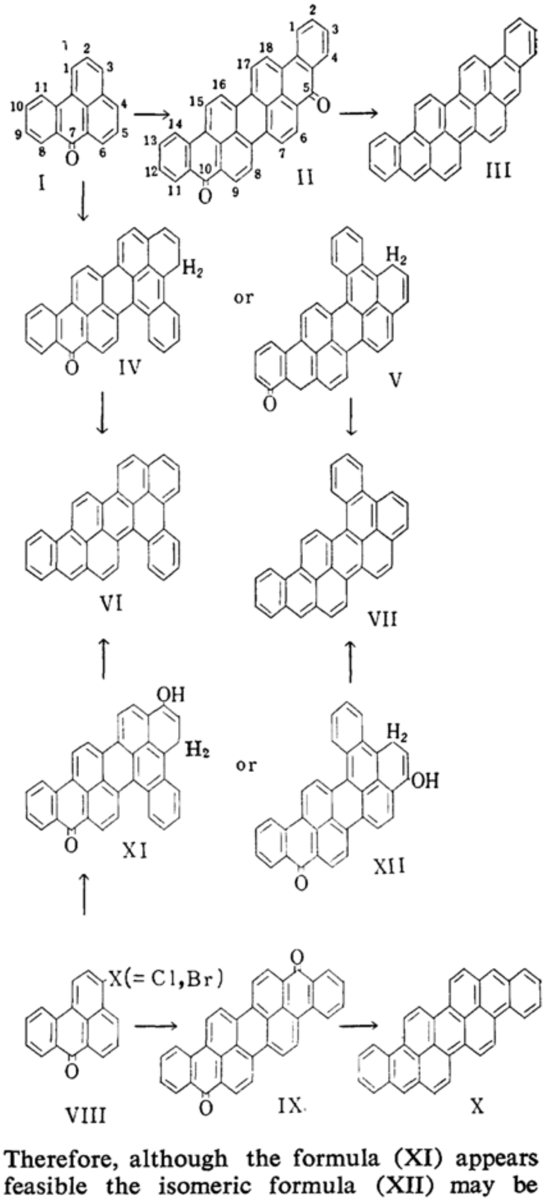
As described in a previous paper[1], the reduction of violanthone B resulted in obtaining the new condensed aromatic hydrocarbon, violanthrene B. Generally, when the method of alkali fussion on benzanthrone (I) derivatives (except 3-position) is applied for the purpose of obtaining the vat dyes of the violanthron (II) series, the B-compound is by-produced with violanthrone derivatives. For example, 4, 11- and 1, 14-dimethoxyviolanthrone were prepared from 8- and 11-methoxybenzanthrone respectivery by alkali fusion, and B-compounds were also obtained[2]. Violanthrone B and these B-componds resemble each other in their vattability and in their coloration with concentrated sulfuric acid. It is, therefore, suggested that the B-compounds by-produced with A-compounds of the violanthrone A type may be derivatives of violanthrone B.

Further, Nagai and Masuda have reported that the 6-position of benzanthrone contributes to the formation of B-compound because the reaction of the alkali fusion of 6-phenylbenzanthrone produces A-compound, but not B-compound[3]. According to these facts, the formula VI or VII can be applied to the skeleton of B-compound, which has only one carbonyl group[4].

On the other hand, there is another type of B-compound, that by-produced with isoviolanthrone (IX) from 3-halogenobenzanthrone (VIII) by heating with alcoholic potassium hydroxide. This B-compound, which is as barely vattable as violanthrone B, has been denoted as isoviolanthrone B by Maki and Nagai[5], and they have suggested as the formula XI, in which the halogen atom was converted into the hydroxl group. In addition, Nagai et al. have reported that the reaction of the alcoholic alkali of 3-chloro-6-phenylbenzanthrone produces A-compound of the isoviolanthrone type, but not B-compound[3].



Therefore, although the formula (XI) appears feasible the isomeric formula (XII) may be also considered, as has been mentioned for violanthrone B[6].

The author has tried to reduce isoviolanthrone B to hydrocarbon by the method of

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[1] J. Aoki, This Bulletin, 34, 1817 (1961).

[2] T. Maki, *J. Chem. Soc. Ind., Japan*, 38, 1390 (1935); *Chem. Abstr.*, 30, 2008 (1936); T. Maki and A. Kikuchi, ibid., 43, 763 (1940); *Chem. Abstr.*, 35, 1783 (1941).

[3] Y. Nagai and M. Masuda, *J. Chem. Soc. Ind., Japan*, 47, 529 (1944).

[4] Consequently, violanthrone B may be considered as having the formula IV or V; T. Maki has suggested IV as the formula.

[5] T. Maki and Y. Nagai, *J. Chem. Soc. Ind. Japan*, 37, 493 (1934); *Chem. Abstr.*, 28, 5435 (1934).

[6] These compounds may be considered free radical because of their paramagnetism; therefore, instead of formulas IV, V, XI and XII, those which take off one hydrogen atom should be preferred. See also Ref. 1.

TABLE I. PROPERTIES OF "DIBENZANTHRENES"

	Violanthrene B		Isoviolanthrene B		Violanthrene A		Isoviolanthrene A
Appearance	Orang red		Deep red		Red		Dark red
M. p., °C	344		400～402		478[7]		510[7]
Color in H_2SO_4	Green		Yellow green		Green		Yellow green
Solubility		>[8]		>		>	
Alcohol	Insol.		Insol.		Insol.		Insol.
Benzene	Hardly sol.		Hardly sol.		Hardly sol.		Hardly sol.
o-Dichloro-benzene	Sol. in hot		Sol. in hot		Hardly sol.		Hardly sol.

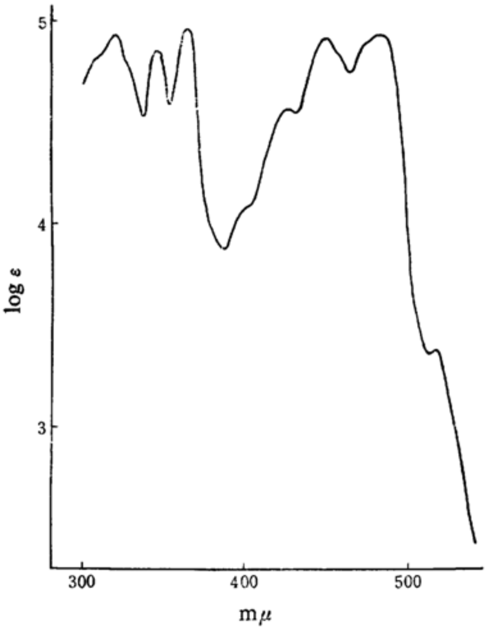

Fig. 1. Absorption spectrum of Violanthrene B (in benzene).

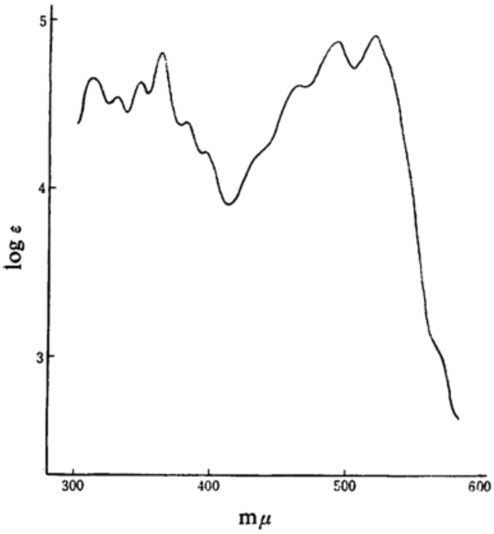

Fig. 2. Absorption spectrum of isoviolanthrene B (in benzene).

zinc dust fusion in order to find the structural formula of this compound. The hydrocarbon obtained from the above method recrystallized from *o*-dichlorobenzene in deep red needles. The meting point of this compound was 400～402°C (uncorr.), and its absorption spectrum was different from that of violanthrene B, as is shown in Figs. 1 and 2. In addition, the properties of this new hydrocarbon, which is called by the author isoviolanthrene B, are quite different from those of violanthrene B, violanthrene A (III) and also isoviolanthrene A (X), as is shown in Table I.

From these facts, we can draw the following conclusions: there are only two types of B-compound, with skeletons assumed to be the fosmulas VI and VII; one of them is violanthrene B and the other is isoviolanthrene B.

Experimental

Isoviolanthrone A (IX) and Isoviolanthrone B.—A mixture of 40 g. of potassium hydroxide, 25 g. of phenol, 15 g. of ethanol and 10.0 g. of 3-chlorobenzanthrone was refluxed with stirring for 2 hr. Then the mixture was treated by the method described in Ref. 5. The yield of isoviolanthrone A was 3.2 g., and this substance is soluble in concentrated sulfuric acid, giving a blue green color. Isoviolanthrone B was obtained as the product, barely vattable and insoluble in glacial acetic acid. In the concentrated sulfuric acid solution it shows as a dark violet color. Yield, 3.0 g. of violet black powder. This sample was once more treated with an alkaline hydrosulfite solution, dissolved in hot chlorobenzene and, after hot filtration, deposited by concentrating the filtrate.

Found: C, 88.80; H, 3.58. Calcd. for $C_{34}H_{18}O_2$ (XI or XII): C, 89.06; H, 3.95%.

Isoviolanthrene B.—A fine powder of 1.00 g. of isoviolanthrone B was kept with 1.0 g. of zinc dust in the mixed flux of 5 g. of zinc chloride and 1 g. of sodium chloride at 260～280°C for 30 min. Then the mixture was treated with 300 ml. of water and the insoluble part filtered off. To remove the excess of zinc dust, it was suspended with 100 ml. of water, and 30 ml. of concentrated hydrochloric acid was added. After being kept overnight, the insoluble part was collected and washed neutral. The crude

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[7] E. Clar, *Ber.*, 76, 456 (1943).

[8] This symbol defined a solubilization power.

reduction product (0.80 g.) was sublimated in a high vacuum ($10^{-3}\sim10^{-4}$ mmHg), and recrystallized from *o*-dichlorobenzene, giving deep red fine needles, m. p. 400~402°C (uncorr.). This product is soluble in organic solvent, giving off a strong fluorescence, and in a concentrated sulfuric acid solution shows at first as green and then as a yellow green, after which it changed no more.

Found: C, 95.56; H, 4.34. Calcd. for $C_{34}H_{18}$ (VI or VII): C, 95.75; H, 4.25%.

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