

A Method of Synthesizing Pure Violanthrene

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Zinc dust fusion is a convenient and excellent method for obtaining aromatic hydrocarbons from their quinones.¹⁾ The preparation of violanthrene (III) from violanthrone (II) is a mere application of the above method, but little attention has been paid to the purity of violanthrone. This quinone as usually supplied is one of the condensation products obtained by the alkali fusion of benzanthrone (I). It is, therefore, unavoidable that by-products²⁾ are mixed in it as impurities. Among these by-products, violanthrone B and all the other substances except isoviolanthrone (IV) can be removed by means of the differences in their solubility and vattability, but the removal of isoviolanthrone is very difficult since isoviolanthrone is as vatable at 55~60°C and as difficult to dissolve in organic solvent as is violanthrone. Although the proportion of isoviolanthrone decreases as the temperature of alkali fusion is raised,³⁾ it has been found by the author that, even in a sample prepared under proper conditions, 6~7 per cent of the sample is isoviolanthrone.⁴⁾

When the zinc dust fusion was applied to such a sample, isoviolanthrone was also reduced to isoviolanthrene (V). In consequence, a mixture of violanthrene and isoviolanthrene was obtained as the reduction product; the separation of these two hydrocarbons was also very difficult. It may, therefore, be asserted that, in seeking to obtain pure violanthrene, such material must not be used.

The reliable sample of pure violanthrene which had been prepared by the present author from pure violanthrone synthesized by Scholl's method⁵⁾ (Scheme 1) gave the absorption spectrum shown in Fig. 1. It has one high peak at 496 m μ , and the peak at 365 m μ is lower than that at 385 m μ . On the other hand, the absorption spectrum of isoviolanthrene has two high peaks, at 363 and 521 m μ (Fig. 1).

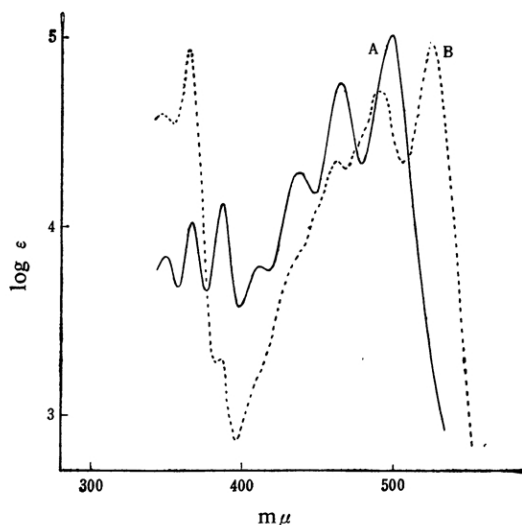


Fig. 1. Absorption spectra of violanthrene (A) and isoviolanthrene (B) (in 1,2,4-trichlorobenzene).

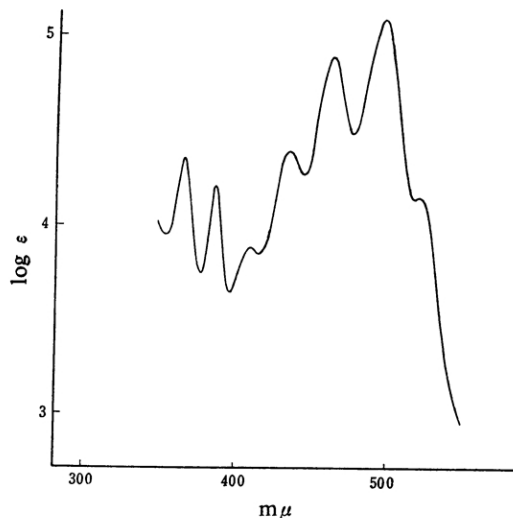
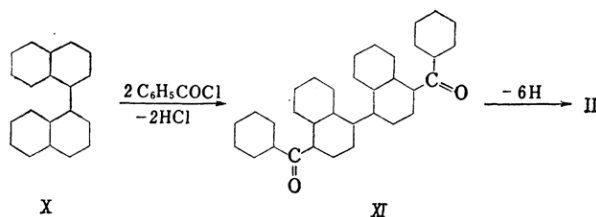
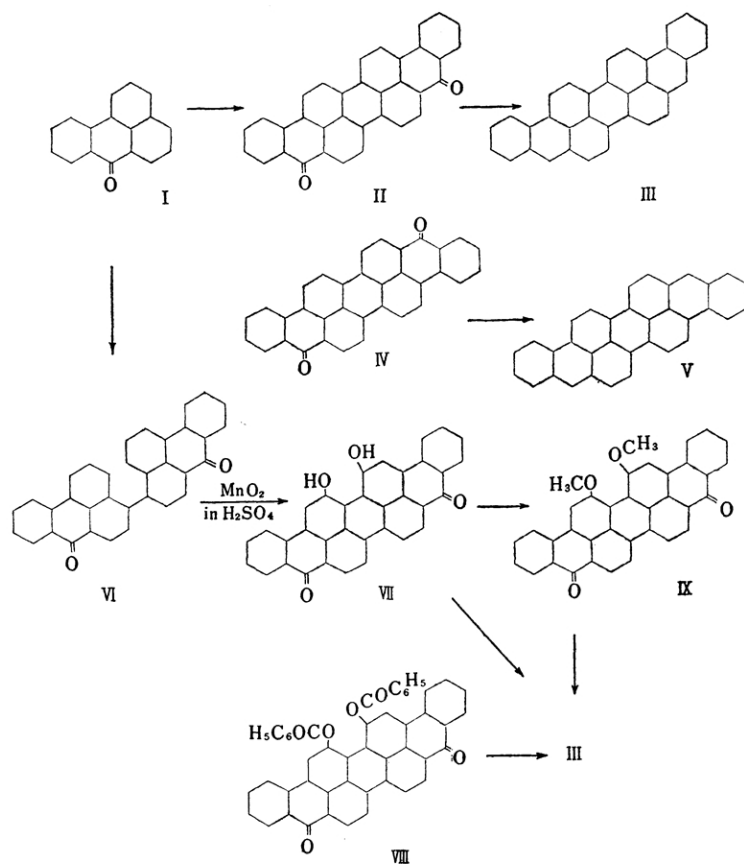


Fig. 2. Absorption spectrum of violanthrene contained isoviolanthrene (in 1,2,4-trichlorobenzene).

- 1) E. Clar, *Ber.*, 72, 1645 (1939).
- 2) Isovianthrone, violanthrone B, 4,4'-dibenzanthronyl (VI), etc.
- 3) This relation was reported by Lüttringhaus and Neresheimer (*Ann.*, 473, 259 (1921)), in which paper it was also stated that isovianthrone was not produced under the proper conditions (220~230°C).
- 4) J. Aoki, Y. Usui, and S. Fujisawa, Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.
- 5) R. Scholl and Chr. Seer, *Ann.*, 394, 171 (1912).

However, the absorption spectrum of the reduction product obtained from violanthrone containing isoviolanthrene was very characteristic, as is shown in Fig. 2. As a result of the



presence of isoviolanthrene, it has a low peak at nearly $520\text{ m}\mu$, and the peak at nearly $365\text{ m}\mu$ is unexpectedly higher than that at nearly $385\text{ m}\mu$. These facts confirm that violanthrene, the material needed to obtain pure violanthrene, must be supplied by means of Scholl's method, not by alkali fusion.

However, Scholl's method, which was devised for the determination of the structure of violanthrene, is not an adequate synthetic method, since it consists of many steps and contains processes difficult to perform.

The present author has found, however, that the zinc dust fusion of 16,17-dihydroxyviolanthrone (VII),⁶⁾ its dibenzoate (VIII) and a dimethyl ether (IX) gives pure violanthrene.

Since the dimethyl ether, 16,17-dimethoxyviolanthrone, is a component of "Indanthrene Brilliant Green FFB" and since 16, 17-dihydroxyviolanthrone is its intermediate product, these substances can be readily supplied.

Consequently, the above facts indicate an advantageous method of synthesizing pure violanthrene; the author especially recommends the use of the dibenzoate of 16,17-dihydroxyviolanthrone, since this substance can be readily purified by recrystallization.

6) This substance should be prepared from 4,4'-dibenzanthronyl (VI), as will be described below. Although it is obtained by the oxidation of violanthrone, the purity of the raw material is again questionable.

7) C. S. Schoepfle, *J. Am. Chem. Soc.*, **45**, 1569 (1924).

8) T. Maki and M. Maezawa, *This Bulletin*, **28**, 77 (1955).

In addition, judging from the facts that these materials are applied to obtain the pure sample of violanthrene, it may be considered that these substances contain little or no isomer of the isoviolanthrene type, because the cyclization of 4,4'-dibenzanthronyl is carried out by the action of manganese dioxide in a concentrated sulfuric acid, not by alkali fusion.

Experimental

Violanthrene (II) (Scholl's Method).—This material was synthesized in the steps shown in Scheme 1. Dinaphthyl (1,1') (X) was prepared from α -bromonaphthalene by the method described in Ref. 7. From this product, violanthrene was synthesized following Scholl's method.⁹⁾ The crude product was refluxed with 100 parts of chlorobenzene for 2 hr., and the soluble impurities were removed by hot filtration. Further purification was carried out by the vatting method. Thus pure violanthrene was obtained.

Yield: 0.6 g. of II from 1.0 g. of XI, 1.6 g. of XI from 2.5 g. of X, and 3.2 g. of X from 50 g. of α -bromonaphthalene.

16, 17-Dihydroxyviolanthrene (VII).—The synthesis was carried out by the method described in Ref. 8.

Dibenzoate (VIII).—A mixture of 2.0 g. of VII, 2.0 g. of pyridine and 200 g. of *o*-dichlorobenzene was refluxed for 30 min. Then, 4.5 g. benzoyl chloride was added, and boiling was continued for 30 min. After standing overnight, the reaction mixture was filtered to remove the unchanged substance as the insoluble material (0.9 g.). The filtrate was slightly warmed and 100 ml. of alcohol added, giving fine black needles with a certain green brightness. Yield: 1.5 g.; m. p. higher than 400°C.

This product, 16,17-dibenzoate, is soluble in an organic solvent; the solution shows a purple color with a strong red fluorescence. In addition, as a result of the examination of the above method, it was found that pyridine was indispensable for this reaction and that more of it was necessary than the mole ratio of benzoyl chloride.

Found: C, 82.58; H, 3.53. Calcd. for $C_{48}H_{24}O_6$ (VIII): C, 82.75; H, 3.47%.

16, 17-Dimethoxyviolanthrene.—“Indanthrene Brilliant Green FFB” (Mitsui Chemical Industries Ltd.) was refluxed with 50 parts of 96, 60 and 20 % alcohol successively; the insoluble part was then collected, washed with water, and dried. This material, after the water-soluble substances had been removed, was finely powdered, refluxed with 100 parts of chlorobenzene for 2 hr. and the insoluble part used as the sample.

Zinc Dust Fusion (Violanthrene).—Violanthrene or its derivative was treated as in Ref. 9.

The sample of Fig. 2 was prepared from impure violanthrene (violanthrene 92.7, isoviolanthrene 7.3 %¹⁰⁾); by comparing the absorption spectra, the amount of isoviolanthrene in this reduction product was estimated at about 10 per cent.

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9) J. Aoki, This Bulletin, 34, 1818, 1821 (1961).

10) This value was obtained from the absorption spectra in concentrated sulfuric acid. The details will be dealt with in a later report.