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Condensation Products of Benzanthrone Obtained Using Copper Powder and Fused Zinc Chloride

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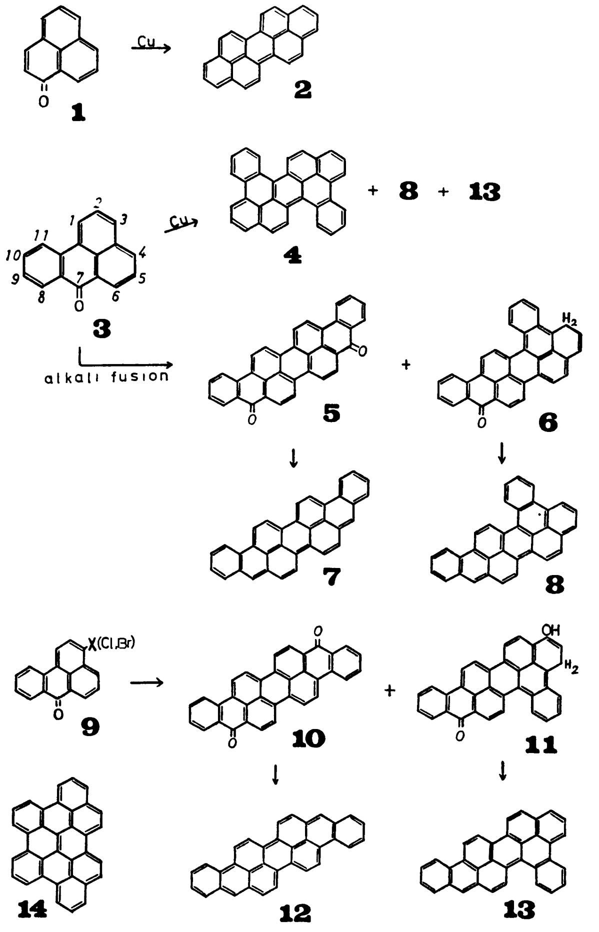
Synopsis. By heating benzanthrone (**3**) with copper powder, zinc chloride, and sodium chloride, violanthrene B (**8**) and isoviolanthrene B (**13**) were obtained in addition to the tetrabenzo[*a, cd, j, lm*]perylene (**4**) reported previously. This method may be considered to be a convenient method of synthesizing not only **4**, but also **13**.

Previously, Aoki reported[1] that 1-phenalenone (**1**) and benzanthrone (**3**) gave dibenzo[*cd, lm*]perylene (**2**) and tetrabenzo[*a,cd,j,lm*]perylene (**4**), respectively, upon heating with copper powder in a mixed flux of zinc chloride and sodium chloride. However, in the case of **3**, other compounds are possibly produced by coupling at positions other than the carbonyl carbon atom. In this paper, the results of a reinvestigation of work reported in Ref. 1 are reported.

By elution chromatography of the reaction products, a small amount of violanthrene B (**8**)[2,4] and a considerable amount of isoviolanthrene B (**13**)[3-5] were isolated along with **4**, and small amounts of unidentified materials.



On the other hand, however, alkali fusion, the typial condensation method for ketones such as **3**, gives violanthrones[6] (**5**, **6**;[6b] **10**, **11**[6c]). Since the carbonyl group remains, the Clar reduction method[7] must be applied in order to obtain the hydrocarbons (**7**, **8**; **12**, **13**).[2,3] Futhermore, no reports have been published concerning the formation of products having a 4-type skeleton.

In the present work, the above unidentified materials were not obtained in a pure state, but they were considered to be present in a mixture with a few hydrocarbons.[8] Consequently, the present method produces hydrocarbons in a single step from **3**, but affords no A-type substances (**5**, **7**, **10**, **12**).[9] This method may be considered to be a convenient method for preparing not only **4**, but also **13**, since it more readily gives pure **13** in a higher yield than the method of reducing **11**.

Experimental

The UV spectra were recorded with a Shimadzu Model D 40 RW Multiconvertible Spectrophotometer.

Dibenzo[*a,cd*]naphtho[3,2,1-*lm*]perylene (**8**) (violanthrene B). The synthesis from **6** has already been reported.[2] Mp 344 °C (corr.), $\lambda_{\max}^{\text{benzene}}$ nm (log ε): 482 (5.00), 451 (4.57), 424 (4.21), 400 (sh., 3.70), 363 (4.69), 345.5 (4.46), 318 (4.63), 305 (4.48).[10]

Dibenzo[*a,cd*]naphtho[1,2,3-*lm*]perylene (**13**) (isoviolanthrene B).[5] Using the Clar method,[3,7] 1.00 g of isoviolanthrone B (**11**) was reduced. The crude product (0.95 g) was sublimated at high vacuum (10^{-3}—10^{-4} Torr), and the yellowish-brown sublimates (0.35 g) were purified by means of recrystallization from benzene and then column chromatography on alumina with benzene, to give 0.05 g of brown-yellow, fine needles. Mp 307 °C (uncorr.), 319 °C (corr.), $\lambda_{\max}^{\text{benzene}}$ nm (log ε): 471 (4.87), 441 (4.55), 415 (4.22), 390 (sh., 3.70), 357 (4.81), 340.5 (4.50), 325 (4.24), 308 (4.76), 294 (4.55).

Found: C, 95.61; H, 4.31%. Calcd for $C_{34}H_{18}$: C, 95.75; H, 4.25%.

Condensation. A mixture of 5.00 g of benzanthrone (**3**), 5.0 g of copper powder, 25 g of zinc chloride and 5 g of sodium chloride was maintained at 230 °C for 30 min, and treated, by a method similar to that reported previously.[1] The crude product (9.85 g) was refluxed with 600 g of xylene for 2 h, and the insoluble part was filtered off after cooling. The filtrate was chromatographed on alumina into several fractions (using xylene as the eluent). The product, obtained by evaporation of successive fractions, were purified by recrystallization and high vacuum sublimation, to give 616 mg of **4**, 56 mg of **8**, 308 mg of recovered **3**, 623 mg of **13**, and 85 mg of reddish-brown crystals. This last material has absorption peaks at about 420, 495, and 530 nm in benzene and appeared to be a mixture of unidentified hydrocarbons[8] not of the A-type (**7**, **12**),[9] however, further purification was very difficult.

That part insoluble in xylene (7.0 g) was refluxed with 200 g of *o*-dichlorobenzene for 2 h, and the insoluble material (5.25 g) was removed by hot filtration. This filtrate was evaporated to dryness, and the residue was chromatographed on alumina with chlorobenzene, and worked up in a manner similar to that used for the xylene filtrate, giving various amounts of the same products described above.

The total amounts and yields of the products were:

tetrabenzo[*a*,*cd*,*j*,*lm*]perylene (**4**)	754 mg	18.1%,
violanthrene B (**8**)	90 mg	2.2%,
isoviolanthrene B (**13**)	833 mg	20.0%,
unidentified material	195 mg	4.7%,
recovered benzanthrone (**3**)	505 mg	10.1%.

References

1) J. Aoki, *Bull. Chem. Soc. Jpn.*, **37**, 1079 (1964).

2) J. Aoki, *Bull. Chem. Soc. Jpn.*, **34**, 1817 (1961).

3) J. Aoki, *Bull. Chem. Soc. Jpn.*, **34**, 1820 (1961).

4) The formulae were indicated as shown in the scheme for the X-ray analysis of the present samples; T. Maekawa, Disertation, The University of Tokyo (1968).

5) Further examination showed that the previous sample[3] was somewhat impure. Reliable results are reported in the present paper.

6) For example, a) A. Lüttringhaus and H. Neresheimer, *Ann.*, **473**, 259 (1929); b) T. Maki, *Kogyo Kagaku Zasshi*, **35**, 1441 (1932); c) T. Maki and Y. Nagai, *ibid.*, **37**, 493 (1934).

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

8) One may be **14**.[1]

9) The unidentified material is readily soluble even in benzene, whereas the A-type hydrocarbons (**7**, **12**) are sparingly soluble although their UV spectra show $\lambda_{\max}$ around 495 and 520 nm, respectively.

10) These spectral data are more plausible than those previously published.[3]