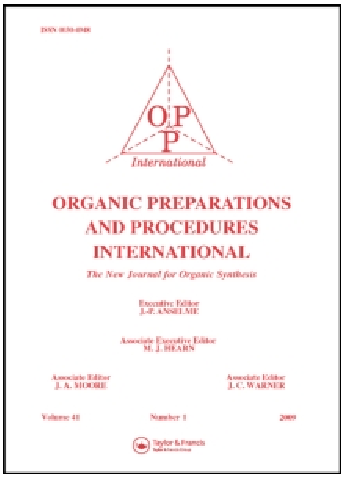

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AN IMPROVED SYNTHESIS OF BENZO[k]FLUORANTHENE

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† Taken in part from the Ph.D. Thesis of J. D. Weaver, Oklahoma State University, July 1973.

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AN IMPROVED SYNTHESIS OF BENZO[k]FLUORANTHENE

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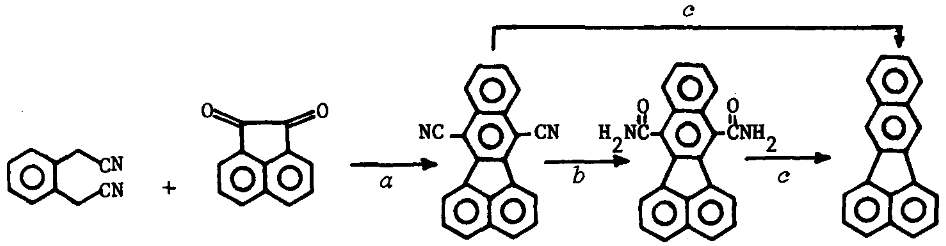
This synthesis of V was reported[1] as proceeding through the diamide IV. We found that the tedious preparation of IV may be omitted to give V in 60% overall yield.



I II III IV V

[a]Piperdine. [b]KOH, $HOCH_2CH_2OH$, Δ. [c]H_3PO_4, Δ.

EXPERIMENTAL

Melting points were uncorrected. IR spectra were recorded on a Beckman IR-5A spectrophotometer. ^1H NMR spectra were recorded at 100.1 MHz on a Varian XL-100A and are reported in terms of δ relative to internal TMS.

7,12-Dicyanobenzo[k]fluoranthene.- A solution of o-phenylenediacetonitrile (I) (67 g, 0.43 mol), acenaphthenequinone (II) (72.5 g, 0.4 mol), and 1100 ml of piperidine was placed in an ice bath for 50 min without stirring, stirred for 40 min at ice bath temperature, and then stirred for 4 hr. at ambient temperature. After 65 hr., the reaction mixture was treated with 8.6 l of 5% hydrochloric acid and filtered. The filter cake was washed with water, recrystallized from 4500 ml of nitrobenzene, and leached with isohexane[2] to yield 88.5 g (74%) of 7,12-dicyanobenzo[k]fluoranthene (III), mp. 357-359° (lit.[1] mp. 357-359°); IR (KBr) 820, 760 cm^{-1}; ^1H NMR ($DCCl_3$) δ 7.60-8.90 (m, 10, ArH).

Benzo[k]fluoranthene.- A mixture of 30 g (0.1 mol) of III and 3000 g of 100% phosphoric acid was stirred for 21 hr. at room temperature, heated to 280° for 18 hr., cooled to room temperature, and poured into 2 l of water. After stirring overnight a benzene extract (1000 ml) was concentrated, the resulting yellow solid was collected by filtration, placed in a Soxhlet apparatus over a bed of alumina[2] and then extracted with 600 ml of isohexane.[3] Concentration to a thick oil yielded 20.5 g (81.3%) of V, mp. 217-

217.3°, lit.[1] 217-217.4°; IR (KBr) 884, 818, 771, 740 cm^{-1}; ^1H NMR (acetone-D_6) δ 7.30-8.24 (m, 10, ArH), 8.48 (s, 2, ArH).

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BENZO[c]PHENANTHRENE

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The route[1] shown was selected as being suitable for preparing several grams of benzo[c]phenanthrene (IV).[1-5] The synthesis proceeded as expected except that we experienced difficulty in removing sulfur from product III. This was overcome by substituting Pd/C (step c). The slight decrease in yield is offset by convenience and time save. We also substituted cuprous oxide and quinoline (step d, 72% yield) for barium hydroxide [lit.[1] yield