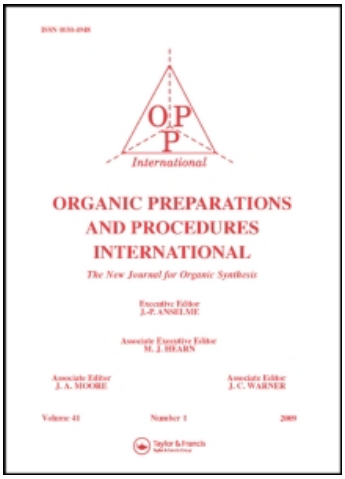

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SYNTHESIS OF BENZ(a)ANTHRACENE-5,6-DIONE

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SYNTHESIS OF BENZ(a)ANTHRACENE-5,6-DIONE

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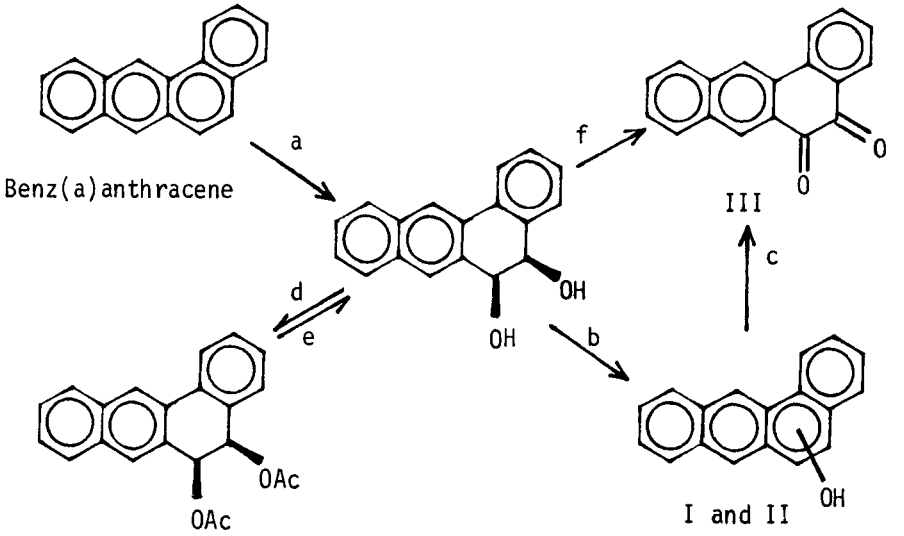
Of several hydroxylated polycyclic aromatic hydrocarbons (PAHs),[1] only 5- and 6-hydroxybenz(a)anthracene (I and II) were readily oxidized to the dione III, a required compound for the metabolic studies of benz(a)anthracene (BA), in 85-92% yields via air oxidation or Fremy's salt. Thus, the synthesis of III from BA via route (a, b, c) represents an improvement over the general sequence[2,3] a, d, e, f which requires four steps and produces inconsistent yields.



a) OsO_4, Pyridine b) HCl, HOAc c) Air oxidation or Fremy's salt
d) Ac_2O, Pyridine e) NH_3, CH_3OH f) Pyridine·SO_3, Et_3N, DMSO

EXPERIMENTAL

Fremy's salt, 1-naphthol and 9-phenanthrol were purchased from Aldrich Chemical Company. All the other hydroxy-PAHs studied were synthesized according to the published procedures.[3-5] Spectral data (ir, nmr and mass spec.) of III were identical to those of an authentic sample.

Air Oxidation of I.- A solution of 5-OH-BA (24.4 mg, 0.1 mmol) in 10 ml of anhydrous acetone was gently bubbled with air at ambient temperature for 6 days. The deep red solids were collected, washed with water and then ethanol and dried. Chromatography on silica gel gave on elution with benzene-ethyl acetate (1:1), 23.2 mg (90%) of dione III as deep red needles. Analytical sample was obtained by further recrystallization from hexane-chloroform, mp. 260-262°, lit.[6] 260-262°.

II was similarly air oxidized to III in 88% yield.

Air Oxidation of Crude I and II.- A mixture of crude I and II obtained via step a followed by step b was air oxidized directly to afford pure III in 85% yield.

Fremy's Salt Oxidation of 5-OH-BA.- To a solution of Fremy's salt (1 g, 3.4 mmol) and potassium dihydrogen phosphate (0.27 g, 2 mmol) was added a solution of 5-OH-BA (0.244 g, 1 mmol) in anhydrous acetone (50 ml). The resulting solution was stirred at ambient temperature overnight. After the workup as before, 0.237 g (92%) of III was obtained.

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