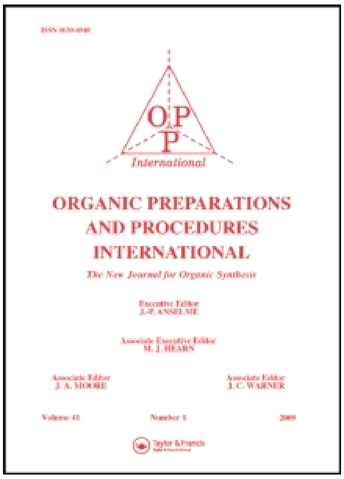

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HIGH-YIELD, ONE STEP PHOTOCHEMICAL SYNTHESIS OF 3- AND 4-BROMOMETHYLBENZOIC ACIDS

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dride, mp. 240-242° (dec.) as a creamy white solid. (Assay by titrimetry: min 98%).

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HIGH-YIELD, ONE STEP PHOTOCHEMICAL SYNTHESIS OF 3- AND 4-BROMOMETHYLBENZOIC ACIDS

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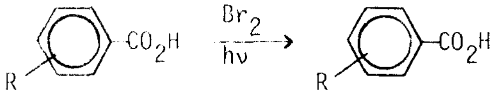
The few reported[1,2] procedures for the preparation of 3- and 4-methylbenzoic acids (II) utilize relatively expensive or unavailable reagents or starting materials or are patents[3,4] for which few details are given. We now report a simple one-step, good yield procedure for the preparation of IIa and IIb.



I
a) R = 3-CH_3
b) R = 4-CH_3

II
a) R = 3-CH_2Br
b) R = 4-CH_2Br

EXPERIMENTAL

4-Bromomethylbenzoic Acid (IIa).- 4-Methylbenzoic acid (12.2 g, 0.090

mol) was dissolved in 200 ml of benzene and the solution brought to reflux in a 2-necked flask provided with an addition funnel and reflux condenser attached to a sodium hydroxide trap for evolved hydrogen bromide. Bromine (5.0 ml, 0.10 mol) dissolved in 100 ml of benzene was added dropwise while the solution was irradiated with a 250 W tungsten lamp. After the addition of bromine was complete, the solution was refluxed for 30 min. Upon cooling to room temperature and then in an ice-water bath, 4-bromomethylbenzoic acid precipitated. The crystals were collected (15 g, 78%), mp. 228°, lit.[2] mp. 229°. Evaporation of the benzene filtrate gave more solid (total yield 90%).

3-Bromomethylbenzoic Acid (IIb).- Bromination of 3-methylbenzoic acid was carried out as above (9.50 g, 0.070 mol of acid, 75 ml of benzene, 4.0 ml, 0.090 mol of bromine). The reaction proceeded more slowly. When the reaction was complete, as indicated by the disappearance of the singlet of the methyl group at δ 2.90, the solution was concentrated *in vacuo* to one-fourth its volume and cooled in an ice-bath. The precipitated product, 3-bromomethylbenzoic acid, was collected and dried in a desiccator (13.5 g, 90% yield). The product was dissolved in hot carbon tetrachloride, an equal volume of petroleum ether (bp. 55-110°) was added and upon cooling the solution in an ice-bath, the acid (11.8 g, 80% yield) crystallized mp. 153°, lit.[3] 155-6°.

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

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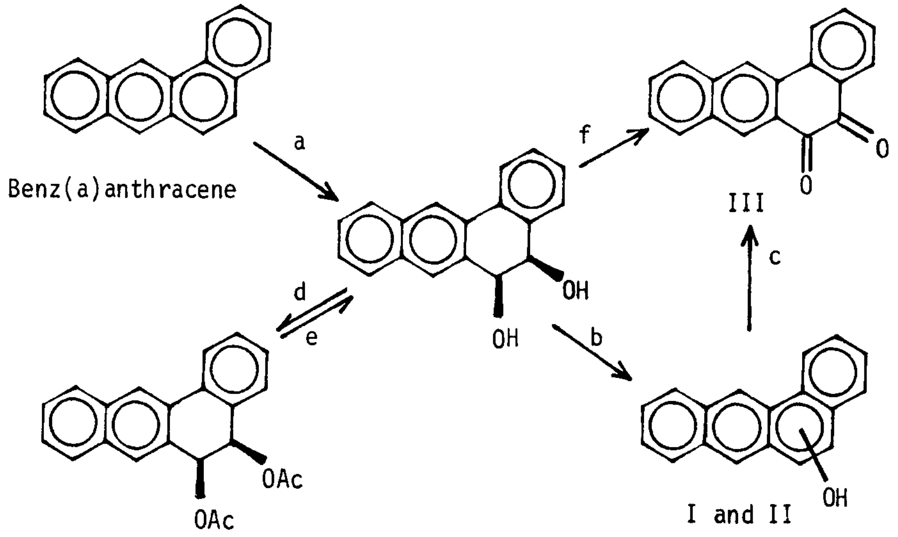
Of several hydroxylated polycyclic aromatic hydrocarbons (PAHs),[1] only 5- and 6-hydroxybenz(a)anthracene (I and II) were readily oxidized to the dione III, a required compound for the metabolic studies of benz(a)anthracene (BA), in 85-92% yields via air oxidation or Fremy's salt. Thus, the synthesis 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