A Synthesis of Phenanthrene by Intramolecular Benzyne Cyclisation

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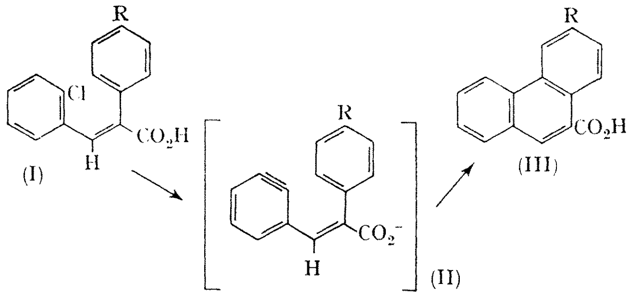
A CONVENIENT synthesis of phenanthrenes has been developed. Condensation of phenylacetic acid with *o*-chlorobenzaldehyde gave *trans*-α-phenyl-2-chlorocinnamic acid (Ia).[1] Reaction of this with an excess of potassium amide in liquid ammonia gave crude phenanthrene-9-carboxylic acid (IIIa) (40%) which, on decarboxylation, gave phenanthrene. Similarly, the *p*-methoxy-analogue (Ib) gave 3-methoxyphenanthrene-10-carboxylic acid (IIIb) (55%).



a, R=H; b, R=OMe

The conditions used in this reaction are typical for generation of benzyne intermediates, presence of which is also indicated by the observed characteristic[2] colour changes. Since benzyne is somewhat inert towards benzene[3,†] success of the present cyclisation may be due to forced proximity of the benzene and the aromatic ring. The mechanism[4] and scope of this reaction are under investigation.

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[†] In a forthcoming publication from this laboratory it will be shown that intramolecular benzyne cyclisation proceeds readily with especially activated benzene rings.

[1] DeLos F. DeTar and Yun-Wen Chu, *J. Amer. Chem. Soc.*, 1955, **77**, 4410.

[2] J. F. Bunnett and Joseph A. Skorcz, *J. Org. Chem.*, 1962, **27**, 3839.

[3] R. G. Miller and Martin Stiles, *J. Amer. Chem. Soc.*, 1963, **85**, 1798.

[4] Some earlier reported high-temperature cyclisations may also proceed through benzyne-type intermediates; C. L. Hewett, *J. Chem. Soc.*, 1938, 1286.

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