Photochemical Cyanation of Aromatic Hydrocarbons with Cyanide Anion

By Kazuhiko Mizuno,* Chyongjin Pac, and Hiroshi Sakurai
(*The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka, Japan*)

Summary The efficient photo-cyanation of phenanthrene and naphthalene with sodium cyanide in the presence of 1,4-dicyanobenzene is reported.

The photochemical nucleophilic substitution of aromatic compounds, especially nitro-compounds, has been extensively investigated[1] and can be used for the preparation of aromatic compounds. However, photoaddition of nucleophiles to aromatic hydrocarbons is not so well known.[2] We report here the efficient photo-cyanation of phenanthrene and naphthalene with cyanide anion in the presence of water and 1,4-dicyanobenzene.

Irradiation of an *NN*-dimethylformamide (DMF)–water (3:1) solution containing phenanthrene (600 mg) and NaCN (3 g) in the presence of 1,4-dicyanobenzene (120 mg) through Pyrex by a high-pressure mercury arc gave 9-cyanophenanthrene, m.p. 107—108 °C (40 mg, 6%), 9-cyano-9,10-dihydrophenanthrene, m.p. 82—83 °C (315 mg, 49%), and a mixture of the dimer of 9-cyanophenanthrene and dicyanated compounds (150 mg).† The presence of both water and 1,4-dicyanobenzene is essential for the photo-cyanation; in the absence of 1,4-dicyanobenzene, the photo-cyanation occurs only with $\leqslant 1/15$th efficiency in comparison to that in the presence of 1,4-dicyanobenzene, and cyanodihydrophenanthrene is not formed in the absence of water though a small amount of 9-cyanophenanthrene was produced. In the absence of NaCN, moreover, irradiation gave no products, and phenanthrene and 1,4-dicyanobenzene were recovered.

Similarly, irradition of a DMF–water (3:1) solution of naphthalene and NaCN in the presence of 1,4-dicyanobenzene afforded monocyanated compounds (30%)‡ and dicyanotetrahydronaphthalene (15%). Aromatisation of the monocyanated compounds with Pd–charcoal gave 1-naphthonitrile in excellent yield, while 2-naphthonitrile was not detected. Photocyanation of anthracene also occurs to give 9-cyanoanthracene, m.p. 179 °C.

The essential role of 1,4-dicyanobenzene in the photocyanation suggests that direct nucleophilic attack of cyanide anion on the excited hydrocarbons is unfavourable; the photocyanation could reasonably be interpreted in terms of nucleophilic attack of cyanide anion on cation radicals of the aromatic hydrocarbons which are generated by electron transfer from excited hydrocarbons to 1,4-dicyanobenzene.§

(*Received, 7th April* 1975; *Com.* 396.)

---

† Percentage yields are based on unrecovered hydrocarbons. The 1,4-dicyanobenzene was also consumed as the conversion increased.

‡ Composed of 1-cyanodihydronaphthalene isomers, 1-naphthonitrile and other compounds.

§ U.v. spectral measurements showed no indication of the formation of charge-transfer complexes in the ground state.

[1] E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, 1968, **16**, 137; J. A. J. Vink, P. L. Verheijdt, J. Cornelisse, and E. Havinga, *Tetrahedron*, 1972, **28**, 5081; G. G. Wubbels and R. L. Lestinger, *J. Amer. Chem. Soc.*, 1974, **96**, 6698.

[2] J. A. J. Vink, C. M. Lok, J. Cornelisse, and E. Havinga, *J.C.S. Chem. Comm.*, 1972, 710; S. Nilsson, *Acta Chem. Scand.*, 1973, **27**, 329.