Light-induced Ethylation of Dicyanobenzenes with Triethylamine

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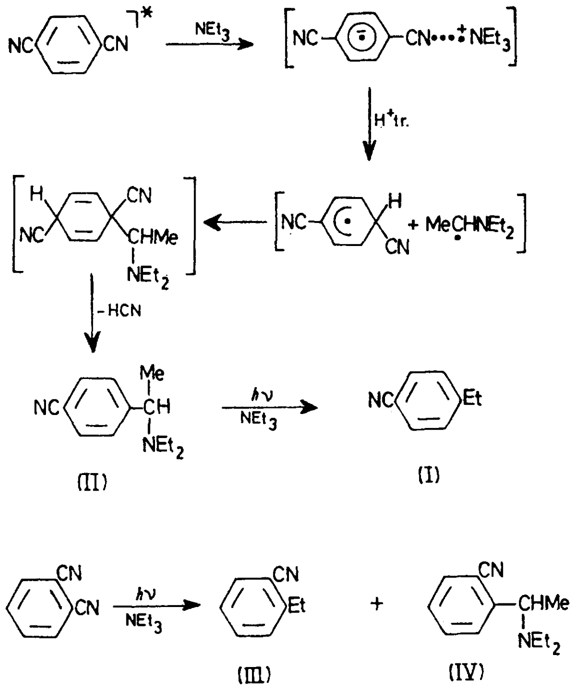
Summary Irradiation of *o*- and *p*-dicyanobenzenes in the presence of triethylamine gave *o*- and *p*-ethylbenzonitriles respectively along with some substitution products.

THE 1,4-photoaddition of aliphatic tertiary amines to benzene has been reported by Bryce-Smith *et al.*[1] We now report that irradiation of dicyanobenzenes in the presence of triethylamine furnishes ethylbenzonitriles *via* addition, followed by elimination, and then reduction.

Irradiation of a mixture of *p*-dicyanobenzene (0·05 M) and triethylamine (0·5 M) in acetonitrile with a low-pressure mercury arc for 6 h gave *p*-ethylbenzonitrile (I), in 56% yield together with the substitution product (II; 18%).



Scheme

Similarly, irradiation of *o*-dicaynobenzene under similar conditions gave *o*-ethylbenzonitrile (III; 9%) and the substitution product (IV; 79%). No comparable reaction occurred, on the other hand, with *m*-dicyanobenzene. Identifications of (I) and (III) were confirmed by conventional alternative syntheses and (II) and (IV) were identified by mass spectrometric, n.m.r., and i.r. data.

To identify the route leading to (I), (II) was irradiated in the presence of triethylamine and (I) was obtained in good yield, indicating that a novel photo-induced Birch reduction had taken place during the reaction. Participation of a proton-transfer step in the addition of triethylamine to *p*-dicyanobenzene was clarified by the use of a proton donor;[1] the same reaction in the presence of methanol gave the starting material quantitatively. This result is in sharp contrast to results with benzene–triethylamine[1] or tetracyanoquinodimethane–toluene[2] but is similar to tetracyanobenzene–toluene case[3], suggesting the involvement of a proton-transfer step. Oxygen also inhibited the reaction; when the reaction was carried out with oxygen bubbling through the mixture, *p*-cyanobenzamide (1%) was obtained, but with no (I) or (II).

By analogy with the mechanism of photoaddition of triethylamine to benzene[1] and naphthalene,[4] we suggest that the reaction takes place as in the Scheme.

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[1] D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, and C. Manning, *Chem. Comm.*, 1971, 916.

[2] K. Yamasaki, T. Yonezawa, and M. Ohashi, *J.C.S. Perkin I*, 1975, 93; *J.C.S. Chem. Comm.*, 1973, 9.

[3] A Yoshino, K. Yamasaki, T. Yonezawa, and M. Ohashi, *J.C.S. Perkin I*, 1975, 735; *Chem. Comm.*, 1971, 97.

[4] J. A. Barltrop and R. J. Owers, *Chem. Comm.*, 1970, 1462; J. A. Barltrop, *Pure Appl. Chem.*, 1973, **33**, 179.