Photochemical Reactions of Methoxybenzenes with Acrylonitrile

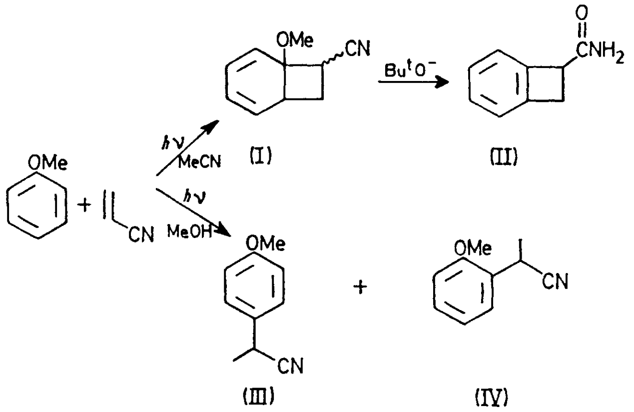
By Mamoru Ohashi,* Yoshio Tanaka, and Shuzo Yamada
(*Department of Materials Science, The University of Electro-communications, Chofu, Toyko* 182, *Japan*)

Summary Irradiation of a mixture of anisole and acrylonitrile in acetonitrile and in methanol gave [2 + 2]cycloadducts and cyanoethylated products, respectively, while irradiation of dimethoxybenzenes in the presence of acrylonitrile in methanol and in acetonitrile gave the corresponding cyanoethylated products and only dimers of acrylonitrile.

Recently charge-transfer type photochemical reactions of aromatic compounds with electron deficient olefins have been extensively studied from synthetic and mechanistic viewpoints.[1] We have previously reported a charge-transfer induced cycloaddition of benzene–acrylonitrile–zinc chloride complexes[2] and we now report photochemical reactions of anisole and dimethoxybenzenes with acrylonitrile.

On irradiation of a solution of anisole (0·10 M) and acrylonitrile (1·0 M) in acetonitrile with a 10 W low pressure mercury lamp for 24 h, the major product was a mixture of stereoisomers of the [2+2] cycloadduct (I) (73%). A similar reaction occurred in EtOAc. Treatment of (I) with $\mathrm{Bu^tOK}$ in $\mathrm{Bu^tOH}$ furnished a cyclobutene derivative (II)[3] in 79% yield, through which the structure of the adduct was confirmed as (I). However, irradiation of a mixture of anisole and acrylonitrile in methanol under similar conditions gave the *para*-α-cyanoethylated product (III)[1] (49%) along with a small amount of the *ortho*-substituted derivative (IV) (10%).

Similarly, irradiation of *o*-dimethoxybenzene in the presence of acrylonitrile in methanol gave 2-(3,4-dimethoxyphenyl)propionitrile (V) (74%) and 2-(2,3-dimethoxyphenyl)propionitrile (VI) (6%), while in the case of *m*-dimethoxybenzene, 2-(2,4-dimethoxyphenyl)propionitrile (VII) (39%) was obtained. Irradiation of *p*-dimethoxybenzene under similar conditions gave 2-(2,5-dimethoxyphenyl)propionitrile (VIII) (56%). However, on irradiation with acrylonitrile in acetonitrile some consumption of the starting dimethoxybenzenes occurred, but only the acrylonitrile dimers, *cis*- and *trans*-1,2-dicyanocyclobutane,[4] were obtained as isolable products.†



When MeOD was used in place of MeOH as the solvent, incorporation of one deuterium atom into the methyl groups in the cyanoethyl groups of (III)—(VIII) was demonstrated by mass spectrometry. This behaviour is similar to the photosubstitution by acrylonitrile of naphthalene[1] indole,[5] and dimethylaniline[6] reported previously.

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† Structures of the products are determined on the basis of i.r., n.m.r., mass spectrometry, and elemental analyses.

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