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The Diverse Photocycloaddition Reactions of 4-Methoxybenzonitrile: Novel Formation of Azacyclo-octatetraenes

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Azacyclo-octatetraenes are formed photochemically from addition of acrylonitrile or benzonitrile to *p*-methoxybenzonitrile: from the former system *ortho*-cycloadducts are also produced but irradiation of allyl cyanide or *cis*-cyclo-octene with *p*-methoxybenzonitrile yields *para*- and *meta*-cycloadducts respectively.

The photoreactions of arenes having either electron-donor or electron-acceptor substituents have been widely studied and are the subject of numerous publications.1 In contrast the excited-state chemistry of benzenoid compounds which are substituted with both types of groups has received very limited attention and is largely restricted to studies of the emission characteristics of these compounds.² The reasons for this neglect may lie in an assumption that the lowest excited state of such arenes would be predominantly of charge-transfer character resulting from intramolecular electron transfer,³ and thus would be unreactive in benzene-type photoprocesses which mainly involve the $S_1 \pi \pi^*$ state.⁴ We have, however, observed that the arenes 4-methoxybenzonitrile and methyl 4-methoxybenzoate are very photolabile in the presence of a variety of ethenes and with certain nitriles yield azacyclo-octatetraenes.

Irradiation (254 nm) of 4-methoxybenzonitrile (0.2 M) in acrylonitrile to 60% consumption of the arene quantitatively produced three 1 : 1 photoadducts of the starting materials in a ratio of 2 : 7 : 1 (relative retention on Carbowax 20M). The last

two isomers were isolated as their N-phenylmaleimide Diels-Alder adducts (m.p. 233-235 and 256-258 °C, respectively) and from their assigned structures,† the two photoproducts are deduced to be the ortho-cycloadducts (1) and (2) respectively. The adduct isomer with the shortest retention time was isolated pure by flash chromatography as orange crystals (m.p. 55-56 °C). This 1:1 adduct was assigned an azacyclo-octatetraene structure on the basis of spectroscopic evidence and structure (3) was confirmed for the product from an X-ray crystallographic determination of a single crystal which gave the following data. The crystals are monoclinic, space group $P2_1/n$, a = 10.226(8), b = 8.187(9), c =12.624(11) Å, $\beta = 101.1(1)^\circ$, U = 1036.9 Å³, Z = 4, $D_m =$ 1.20(1), $D_c = 1.20$ g cm⁻³. 1036 Independent reflections above background were measured on a diffractometer and the structure was refined (N, C, O anisotropic, H isotropic) to

⁺ Structural assignments are deduced from spectral data and their comparison with those of benzene-ethene adducts of known structure; all compounds described here gave satisfactory analytical data.



R 0.067.‡ The structure consists of discrete molecules of (3) as shown in Figure 1. The dimensions of the molecule are as expected. The conformation of the ring shows atoms N(1), C(2), C(5), C(6) coplanar and atoms C(3), C(4), C(7), C(8) coplanar both within 0.02 Å. The two planes are 0.81 Å apart and approximately parallel [angle of intersection 2.2(1)°].

Formation of (3) represents the first example of photocycloaddition of a nitrile function to an aromatic ring, but experiments with other nitriles and arenes show that surprisingly this process is restricted to systems in which the arene has both electron-acceptor and -donor substituents and the nitrile is conjugated; irradiation of benzonitrile and 4-methoxybenzonitrile gives (4), and (5) is formed from acrylonitrile and methyl 4-methoxybenzoate. Prolonged irradiation of the acrylonitrile-4-methoxybenzonitrile system gave (3) and the cyclo-octatriene isomers of (1) and (2), and irradiation at wavelengths longer than 290 nm rapidly produced large amounts of a white insoluble acrylonitrile polymer; the photopolymerisation could be initiated by concentrations <0.006 m of the arene.

Irradiation (254 nm) of 4-methoxybenzonitrile in ethyl vinyl ether gave the two *ortho*-cycloadducts (6) and (7)^{\dagger} in a respective ratio of 1:1.75 but with *cis*-cyclo-octene as the



Figure 1. X-Ray structure of the adduct (3).

addend, the *meta*-cycloadduct (8)[†] was essentially the sole product. Quantum yields for arene disappearance in the above quantitative photoaddition processes were of the order of 0.4 but its reaction in allyl cyanide was very slow and produced three photoadduct isomers (M^+ , m/z 200) in a 1.5:2:3 ratio. The prolonged irradiation necessary to obtain isolable amounts of product destroyed the two more minor components and gave the *para*-cycloadduct (9)[†] in >98% purity. In contrast with these results, only *ortho*-cycloadducts were produced from these three ethenes and methyl 4-methoxybenzoate. It is also noteworthy that the *ortho*- and *meta*isomers of these arenes have absorption spectra markedly different from those of the *para*-isomers,^{2a} and are appreciably more photostable in the presence of the ethenes.

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[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.