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THE [2+2]CYCLOADDITION VS SUBSTITUTION IN PHOTOCHEMICAL REACTIONS OF METHOXYBENZENE-ACRYLONITRILE SYSTEMS

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The mode of photochemical reactions of olefins with aromatics is affected by various factors and currently of considerable interest.1) For instance, McCullough and his co-workers have extensively examined the [2+2]photocycloaddition and substitution of acrylonitrile-naphthalene systems.2) They have pointed out two interesting observations; 1) a protic solvent is necessary for the formation of [2+2]cycloadducts, 2) a correlation exists between electron-transfer energies and the amount of substitution. We have already reported photochemical reactions of anisole with acrylonitrile demonstrating that the [2+2]cycloaddition did occur even in acetonitrile, contrary to their case of acrylonitrile-naphthalene systems.3) We have now examined whether their second observation is valid in methoxybenzene-acrylonitrile analogue systems.

On irradiation of an acetonitrile solution of anisole(0.15 M) and methacrylonitrile(1.0 M) with a low pressure mercury arc for 20 h, the major product was a mixture of stereoisomers of the [2+2]cycloadduct(73%). A similar reaction carried out in methanol yielded the [2+2]cycloadduct(Ib, 38%) plus the *para*-substitution product(IIb, 40%) with a small amount of the *ortho*-substitution product(5%). Likewise, irradiation of anisole in acetonitrile in the presence of crotononitrile gave a mixture of stereoisomers of the [2+2]cycloadduct(Ic) in 74% yield, whereas in methanol the major product was a mixture of the [2+2]cycloadduct(Ic, 67%) and a small amount of the *para*-substitution product(IIc, 6%).

Thus these photochemical reactions of methacrylonitrile and crotononitrile with anisole in acetonitrile are similar to those of acrylonitrile.3) On the other hand, in methanol the anisole-acrylonitrile system gave only the substitution products on irradiation,3) while both anisole-methacrylonitrile and -crotononitrile systems gave the corresponding [2+2]cycloadducts in addition to the substitution products. The amount of substitution products decreases in the order of acrylonitrile > methacrylonitrile > crotononitrile. If it is assumed that the [2+2]cycloaddition proceeds through a singlet exciplex4) and the substitution takes place *via* an ion pair as the intermediate as is the case of naphthalene-acrylonitrile systems,2) that is, the rate-determining step of substitution is electron-transfer from the excited methoxybenzene to the olefin, the trend of substitution in the series of reaction is accounted for in terms of the electron-transfer energies calculated by Weller's equation;[5)]

$$\Delta G = E(D/D^{+}) - E(A^{-}/A) - e_0^{2}/\varepsilon R - \Delta E_{00}$$

Concerning $E(A^{-}/A)$ values House et al. reported that the reduction potential of crotononitrile(54.6 Kcal/mol)[6)] is higher than that of acrylonitrile(52.4 Kcal/mol),[2)] while Houk and Munchausen estimated the electron affinities, which are linearly related to the reduction potentials, of cyanoalkenes being in the order of acrylonitrile > methacrylonitrile > crotononitrile.[7)] Therefore, the exothermic ΔG values in the series of reactions seem to be in the same order which is consistent with the actual trend of substitution. These reaction features are roughly consistent with McCullough's observations, that is, a large amount of substitution occurs if the electron-transfer reaction is exothermic, but when it is endothermic, no substitution products are formed.

A similar tendency is also observed in the case of dimethoxybenzene-acrylonitrile analogue systems. Irradiation of a mixture of methacrylonitrile and o-, m- or p-dimethoxybenzene(DMB) in methanol gave the corresponding substitution product(IIIb, Vb or VIb) in a high yield. Similarly, irradiation of o- or p-DMB in the presence of crotononitrile gave the corresponding substitution product (IIIc or VIc), while in the case of m-DMB, the [2+2]cycloadduct(IVc) and substitution product(Vc) were obtained in 32 and 49% yield respectively. When acetonitrile was used as the solvent, only olefin dimers were obtained as isolable products in the case of o- or p-DMB-methacrylonitrile or -crotononitrile system, while the corresponding [2+2]cycloadducts(IVb or IVc) were also isolated in the m-DMB-methacrylonitrile or -crotononitrile system in 60 or 63% yield respectively. These results as well as those from DMB-acrylonitrile systems[3)] are summarized in the Table.

It is clearly seen from the Table that in the series of DMB-crotononitrile systems the amount of substitution is in the order of o- and p-DMB > m-DMB > anisole. This trend is just reverse to the order of the oxidation potential of the aromatic; anisole(40.6 Kcal/mol) > m-DMB(34.4) > o-DMB(33.4) > p-DMB(30.9).[8)] No mutual comparison of ΔG values in these cases is possible for lack of the exact ΔE_{00} value and the Coulombic term in the reaction conditions. However, the oxidation potentials of the aromatics may indicate the liability of electron-transfer in these reactions.

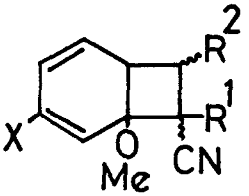
We conclude from these results that the higher the reduction potential(or electron affinity) of the olefin or the lower the oxidation potential of the aromatic is, the larger is the amount of substitution products. these results implies that although participation of the proton-transfer step is revealed by the use of MeOD in place of MeOH as the solvent,[3)] the rate determining step

Table. Yields# of the [2+2]cycloadducts and substitution products[9] in methanol

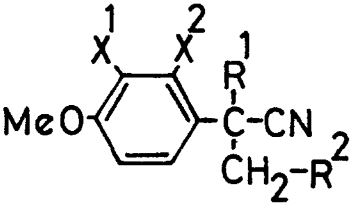
		Acrylonitrile	Methacrylonitrile	Crotononitrile
Anisole	A##	-	Ib 38	Ic 67
	S	IIa 49	IIb 45	IIc 6
o-DMB	A	-	-	-
	S	IIIa 80	IIIb 74	IIIc 71
m-DMB	A	-	-	IVc 32
	S	Va 39	Vb 63	Vc 49
p-DMB	A	-	-	-
	S	VIa 56	VIb 78	VIc 57

\# Percent yield is based on the unrecovered starting methoxybenzene and calculated from g.l.c. analysis.

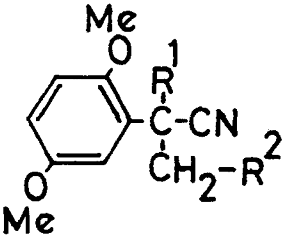
\## A; [2+2]cycloadduct
S; substitution product.



	X	R1	R2
Ib	H	Me	H
Ic	H	H	Me
IVb	OMe	Me	H
IVc	OMe	H	Me

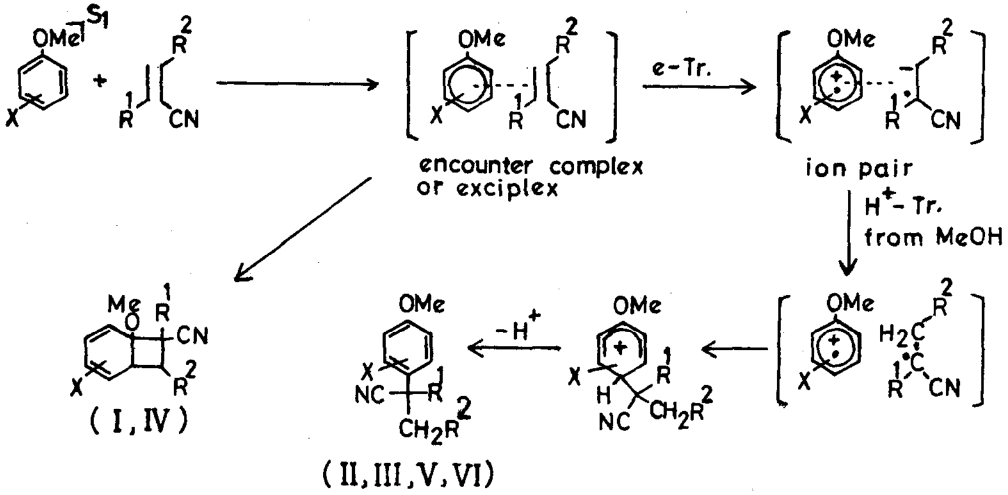


	X1	X2	R1	R2
IIa	H	H	H	H
IIb	H	H	Me	H
IIc	H	H	H	Me
IIIa	OMe	H	H	H
IIIb	OMe	H	Me	H
IIIc	OMe	H	H	Me
Va	H	OMe	H	H
Vb	H	OMe	Me	H
Vc	H	OMe	H	Me



	R1	R2
VIa	H	H
VIb	Me	H
VIc	H	Me

of substitution lies not at the proton-transfer step but at the electron-transfer stage. The following reaction scheme is consistent with the above results.



References and notes

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2) R. M. Bowmann, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, J. Am. Chem. Soc., 96, 692(1974) and references therein.

3) M. Ohashi, Y. Tanaka, and S. Yamada, J. Chem. Soc., Chem. Commun., 1976, 800.

4) Stern-Volmer treatments of the fluorescence quenching of p-dimethoxybenzene with acrylonitrile gave nice linear plots with a $k_q\tau$ value of 18.2 M^{-1}, which indicates that the reaction proceeds through a singlet excited state of p-dimethoxybenzene.

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9) Structures of the products are deduced from spectroscopic data of the isolated materials; UV, IR, NMR, and GC-MS. The GC-MS analysis was most competent to identify the [2+2]cycloadduct or substitution product; the mass spectrum of the [2+2]cycloadduct exhibits a weak molecular ion peak as well as a strong fragment peak(base peak) corresponding to the molecular ion of the starting methoxybenzene, while in the case of substitution product either the molecular ion or $(M\text{-}Me)^+$ peak is the strongest.