

## SOLVENT EFFECTS IN THE PHOTOINDUCED REACTIONS OF NITROAROMATICS WITH CYANIDE ION<sup>1</sup>

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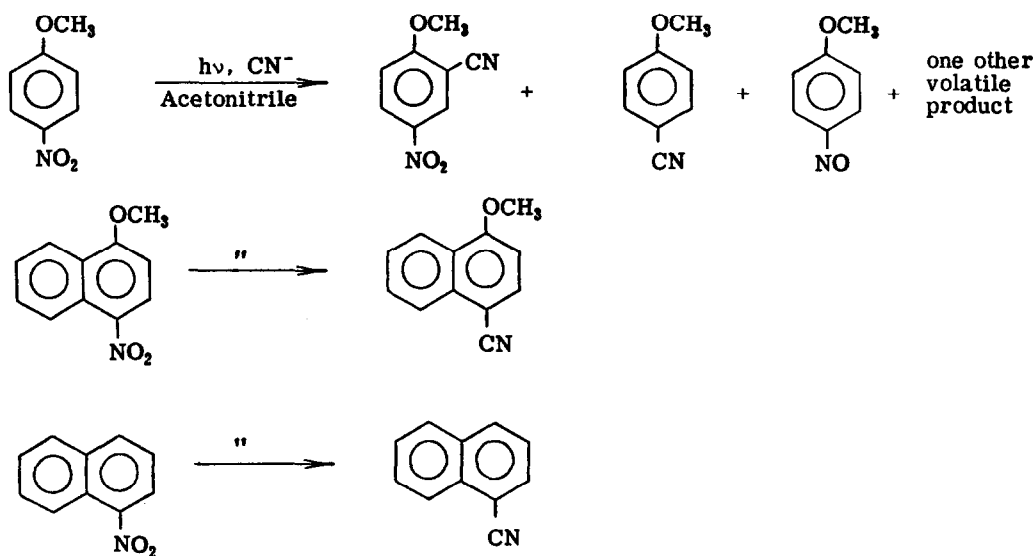
(Received in USA 9 June 1969; received in UK for publication 9 September 1969)

We have found that substituent groups and solvents may have striking effects on the rates of bimolecular reactions involving nucleophiles and photoexcited nitroaromatic compounds. As representative cases, data on reactions of cyanide ion and 4-nitroanisole, 1-nitronaphthalene, and 4-methoxy-1-nitronaphthalene are reported in this communication.

Preparative reactions were carried out with solutions  $10^{-3}$  M in nitroaromatic and  $10^{-2}$  M in cyanide irradiated with a 450 w Hanovia immersion lamp equipped with a Pyrex filter. For quantum yield measurements an Osram 200 w super high pressure lamp was used and a narrow band was selected by a Bausch and Lomb high intensity monochromator.

Photoexcited nitrobenzene does not react with common nucleophiles in dilute aqueous solution;<sup>2</sup> however, photoexcited 4-nitroanisole reacts readily. With cyanide ion in aqueous solution in the presence of air 4-nitroanisole affords 2-cyano-4-nitroanisole in high yield.<sup>3</sup> Accordingly, methoxyl may be considered an "activating" group for photoinduced nucleophilic attack on the nitrobenzene ring. In contrast, we find that methoxyl may serve as a "deactivating" substituent in nitronaphthalene. Thus 1-nitronaphthalene was found to react rapidly on irradiation in an aqueous medium (90% water-10% acetonitrile by vol.) containing cyanide ion ( $10^{-2}$  M). Extraction of the aqueous solution with methylene chloride afforded 1-cyanonaphthalene as the only extractable product (23% yield). Photoinduced displacement of nitro by cyanide has not been heretofore reported, though displacement of nitro by other nucleophiles such as pyridine,<sup>2</sup> hydroxide,<sup>2,4</sup> and piperidine<sup>5</sup> is well established. Under the same conditions 4-methoxy-1-nitronaphthalene did not react with cyanide. The only change produced on irradiation was the very slow disappearance of substrate characteristic of nitroaromatics irradiated in the absence of reactive nucleophiles.

Remarkable changes in reactivity were observed when the solvent was changed to one that was largely aprotic (95% acetonitrile-5% water). In this solvent the reaction of 4-nitroanisole with cyanide was greatly retarded, the quantum yield being about 1/50 that in 90% water-10% acetonitrile. Analysis of the products by vapor phase chromatography revealed five volatile compounds: 2-cyano-4-nitroanisole (9% yield), 4-cyanoanisole (6% yield), 4-nitroanisole (13% yield), 4-nitroanisole (32% recovered), and a substance that was not identified. On the other hand, photoexcited 4-methoxy-1-nitronaphthalene became quite reactive in the acetonitrile solvent. The quantum yield for disappearance of the nitroaromatic was more than 300 times that in 90% water-10% acetonitrile and was dependent on cyanide. 4-Methoxy-1-cyanonaphthalene, the sole organic product detected, was isolated in 70% yield in a preparatory reaction. Finally, it was found that the solvent had little effect on the quantum yield of the photoreaction of 1-nitronaphthalene with cyanide, the ratio in the water and acetonitrile systems being 1.2:1. 1-Cyanonaphthalene was isolated from the reaction in acetonitrile in a yield of 73%. Pertinent quantum yield data are presented in Table 1. Nitrobenzene was unreactive in the acetonitrile



medium as well as in water. Solvent effects have been noted previously for a variety of photochemical reactions of carbonyl compounds;<sup>6,7</sup> however to our knowledge no comparable reversal of reactivity for compounds within a given series has been observed.

TABLE 1. Solvent Effects in Photoinduced Reactions of Nitroaromatics with 0.01 M KCN.

<u>Compound</u>	<u>Solvent</u> <sup>a</sup>	<u><math>\lambda_{\max}</math> (<math>10^{-4} \epsilon</math>)</u>	<u><math>\phi</math></u> <sup>b</sup>
4-Nitroanisole	H <sub>2</sub> O	317 (1.02)	0.32
	CH <sub>3</sub> CN	310 (1.09)	0.0064
1-Nitronaphthalene	H <sub>2</sub> O	342 (0.40)	0.10
	CH <sub>3</sub> CN	334 (0.40)	0.082
4-Methoxy-1-nitronaphthalene	H <sub>2</sub> O	378 (0.83)	0.00015
	CH <sub>3</sub> CN	366 (0.81)	0.047

<sup>a</sup>H<sub>2</sub>O refers to 90% water-10% acetonitrile; CH<sub>3</sub>CN refers to 95% acetonitrile-5% water.

<sup>b</sup>Disappearance of nitroaromatic.

The effect of solvents on the efficiency of photoreduction of aromatic ketones has been ascribed to changes in the energy levels of the  $n, \pi^*$ ,  $\pi, \pi^*$  and C-T excited states of the ketones.<sup>6</sup> Efficient photoreduction is considered to result when the lowest triplet level is predominately  $n, \pi^*$  in character. This hypothesis is supported by spectral data which, in part at least, may be correlated with chemical reactivity. The failure of many nitroaromatic compounds to exhibit emission spectra precludes a corresponding treatment of this class of compounds. By analogy with the aromatic ketones, however, one may organize the photochemistry of the nitroaromatics in a useful manner by assuming that the lowest excited states<sup>8</sup> may likewise be  $n, \pi^*$ ,  $\pi, \pi^*$  and C-T<sup>9</sup> in character and that substituents and solvents influence the relative levels of these states in the same manner as in the case of the aromatic ketones. The experiments described in this communication and a very considerable body of data on other nitro compounds fall into a consistent pattern on the basis that photoreductions of the nitroaromatics involve an  $n, \pi^*$  excited state and photoinduced substitution reactions involve a  $\pi, \pi^*$  excited state.<sup>10</sup> As a rough empirical guide it may be noted that nitro compounds with  $\lambda_{\max}$  300-370 m $\mu$  generally exhibit photoinduced substitution reactions.<sup>11</sup> Decrease in polarity of the solvent may be expected to hinder the substitution reactions of compounds with  $\lambda_{\max}$  near the low wavelength extreme (e.g. 4-nitroanisole, for which the  $n, \pi^*$  and  $\pi, \pi^*$  excited states may be close in energy), to favor the reactions of compounds with  $\lambda_{\max}$  near the high wavelength extreme (e.g. 4-methoxy-1-nitronaphthalene, for which the  $\pi, \pi^*$  and C-T<sup>-</sup> states may be close in energy), and to have little effect in intermediate cases in which the  $\pi, \pi^*$  state is appreciably separated from either the  $n, \pi^*$  or C-T state.

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8. Available evidence indicates that the triplet state is probably involved in the substitution and reduction reactions of excited nitroaromatics. See R. L. Letsinger and K. E. Steller, Tetrahedron Letters, 140 (1969); R. Hurley and A. L. Testa, J. Am. Chem. Soc., 90, 1949 (1968).
9. The C-T state and  $\pi, \pi^*$  states probably represent different degrees of charge separation for a given type of electronic configuration, the C-T state being one of relatively high charge separation, low energy, and low reactivity.
10. R. Hurley and A. C. Testa, J. Am. Chem. Soc., 90, 1949 (1968), have also suggested that photoreduction proceeds through an  $n, \pi^*$  state, and E. Havinga, R. O. de Jongh, and M. E. Kronenberg, Helv. Chim. Acta, 50, 2550 (1967) have proposed a  $\pi, \pi^*$  configuration for the excited state of nitro compounds in substitution reactions.
11. In cases where some group, such as hydroxyl, is present which can lead to deactivation of the excited state, no substitution reactions are observed.