Tetrahedron Letters No. 6, pp 513 - 516, 1974. Pergamon Press. Printed in Great Britain.

THE PHOTOCHEMICAL ADDITION OF ACRYLONITRILE TO IMIDAZOLES[1)]

Yoshikatsu Ito and Teruo Matsuura*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University
Yoshida, Kyoto 606, Japan

(Received in Japan 14 November 1973; received in UK for publication 2 January 1974)

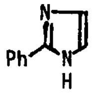
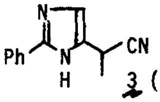
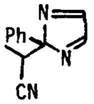
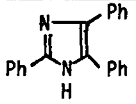
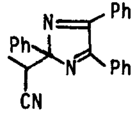
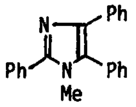
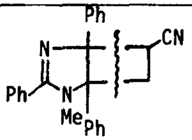
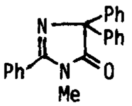
The photochemical reactions of donor-acceptor systems have recently drawn considerable attention. Among them, the photochemical additions of acrylonitrile to aromatic hydrocarbons leading to [2 + 2]cycloaddition and α-cyanoethylation are, in many cases, interpreted in term of exciplex formation.[2)] However, only a few reports on the photochemical addition of acrylonitrile to heteroaromatic systems have appeared.[3,4)] It is now shown that acrylonitrile photochemically adds to an N-unsubstituted imidazole resulting in α-cyanoethylation and to an N-methylimidazole resulting in cycloaddition, possibly via the excitation of a ground state complex.

A solution of an imidazole in acetonitrile or ethanol was irradiated with a high-pressure mercury lamp (Pyrex filter) in the presence of a large excess of acrylonitrile. After a few minutes, the mixture became turbid owing to polymerization of acrylonitrile. Products were separated mainly by chromatographic procedures. The results are shown in Table 1. Under these conditions, 2-phenylimidazole (1) and 2,4,5-triphenylimidazole (2) gave α-cyanoethylated products (3, 4 and 5) in either a protic or an aprotic solvent,[5)] whereas 1-methyl-2,4,5-triphenylimidazole (6) gave cycloadducts 7a and 7b in ethanol and a 5-imidazolone 8 in acetonitrile but no α-cyanoethylated product. These results suggest that the acidic proton of 1 and 2 plays an important role in the formation of α-cyanoethylated products (3, 4 and 5).

For the photochemical formation of 2-(α-naphthyl)- and 2-(β-naphthyl)propionitriles from naphthalene and acrylonitrile in a protic solvent, McCullough et al proposed a mechanism involving the protonation of a naphthalene-acrylonitrile exciplex followed by the collapse of the protonated species to naphthylpropionitriles.[2b)] Possible pathways leading to the photochemical addition of acrylonitrile to imidazoles are shown in Scheme 1.

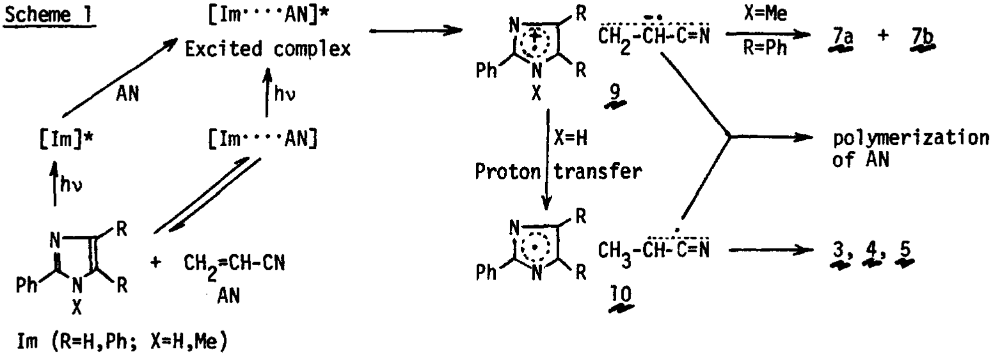
An excited complex, which may be formed by the excitation of a ground state complex between imidazole and acrylonitrile or by the complexing of the excited imidazole to acrylonitrile, is transformed into a radical ion pair 9. With N-unsubstituted imidazoles 1 and 2,

Table 1. Photochemical reaction of imidazoles (Im) and acrylonitrile (AN).

Imidazole	Mol ratio of Im/AN	Solvent	Irradn. time (hr)	Recovered Im (%)	Products (%)
 1	1/17	EtOH	18	96	3 (2.2) 4 (1.3) 
	1/24	MeCN	79	85	3 (2.1) 4 (1.7)
 2	1/210	EtOH	3.5	27	 5 (34)
	1/420	MeCN	4	0	5 (38)
 6	1/270	EtOH	4	77	 7a + 7b (18)[a]
	1/220	MeCN	9	55	 8[6,7] (16)[b]

[a] The ratio of 7a/7b was 3.7. [b] A mixture of cis- and trans-1,2-dicyanocyclobutanes was also obtained.

Scheme 1



the radical ion pair 9 undergoes proton transfer to give a radical pair 10 which finally gives the α-cyanoethylated products (3, 4 and 5). With 1-methyl-2,4,5-triphenylimidazole (6), the radical ion pair 9 collapses to the cycloadducts 7a and 7b. This mechanism is also consistent with the well-known fact the acrylonitrile undergoes both radical and anionic polymerization.[8]

Although there has been no evidence for the ground state-complex formation between acrylonitrile and an aromatic hydrocarbon such as benzene, naphthalene and indene,[2a] we observed the gradual change of the ultraviolet spectra of 1 and 2 with increasing amount of acrylonitrile in ethanol showing isosbestic points (250 and 279 nm for 1 and 271 and 327 nm for 2). This shows the formation of a ground state complex between **1** or **2** and acrylonitrile. Assuming the following equilibrium, the equilibrium constant (K) and the molar absorption coefficient of the 1:1 complex (ε_c) were estimated by the Rose-Drago method.[9)](Table 2). If K is set equal to 0.1 and

$$\mathrm{Im} + \mathrm{AN} \xrightleftharpoons{K} [\mathrm{Im}\cdots\cdot\mathrm{AN}]$$

0.4 for **1** and **2** respectively, the proportion of the complex to the total amount of an imidazole in ethanol under the photolytic conditions is calculated as about 33% and 50% respectively. This demonstrates that the concentration of the complex is high enough to compete with the uncomplexed imidazole for light absorption.[10)]

Table 2. Parameters for the ground state-complex formation between imidazoles and acrylonitrile.

Imidazole	K	ε_c	ε_{Im}	wavelength taken for calculation
2-Phenylimidazole (**1**)	0.04-0.15	9300-11400	12800	265nm
2,4,5-triphenylimidazole (**2**)	0.16-0.55	18900-23000	26000	300nm

The structures of the products were assigned on the basis of spectral and chemical evidences. All products gave satisfactory microanalytical data. Some of their chemical reactions are also described below.

2-[4 (or 5)-(2-phenylimidazolyl)]propionitrile (**3**); mp. 168.5-169.5°; ν_{max}^{Nujol} 2235 cm^{-1} (C≡N); λ_{max}^{EtOH} 270 nm (ε 12400); τ^{CDCl_3} -0.26 (1H, s, disappeared on deuteration, N$\underline{H}$), 2.03-2.83 (5H, m, aromatic H), 2.95 (1H, s, -C$\underline{H}$=), 6.04 (1H, q, J=7Hz, -C$\underline{H}$-CH$_3$), 8.37 (3H, d, J=7Hz, -CH-C$\underline{H}_3$); M/e 197 (M$^+$, rel. int. 76), 182 ([M-CH$_3$]$^+$, 100). This compound was photochemically stable (>280nm in ethanol).

2-[2-(2-phenyl-2H-imidazolyl)]propionitrile (**4**); mp. 76-77°; ν_{max}^{Nujol} 2235 cm^{-1} (C≡N); λ_{max}^{EtOH} 240 (ε 1160), 259 (sh.,640), 265 (sh.,590), 269 nm (sh.,510); τ^{CDCl_3} 1.70 (1H, d, J=5.5Hz, -C$\underline{H}$=)[11)], 1.72 (1H, d, J=5.5Hz, -C$\underline{H}$=)[11)], 2.20-2.77 (5H, m, aromatic H), 6.53 (1H, q, J=7.5Hz, -C$\underline{H}$-CH$_3$), 8.66 (3H, d, J=7.5Hz, -CH-C$\underline{H}_3$); M/e 197 (M$^+$, rel. int. 9), 143 ([M-CH$_3$CHCN]$^+$, 100). Hydrolysis with HCl/EtOH/H$_2$O gave 2-benzoylpropionitrile almost quantitatively Photolysis (>280 nm) in ethanol and LiAlH$_4$ reduction gave **1** (64 and 47% respectively).

2-[2-(2,4,5-triphenyl-2H-imidazolyl)]propionitrile (**5**); mp. 218.5-219.5°; ν_{max}^{Nujol} 2235 cm^{-1}; (C≡N); λ_{max}^{EtOH} 266 nm (ε 7500)[12)]; τ^{CDCl_3} 1.93-2.77 (15H, m, aromatic H), 6.34 (1H, q, J=7.5Hz, -C$\underline{H}$-CH$_3$), 8.56 (3H, d, J=7.5Hz, -CH-C$\underline{H}_3$). Treatment with conc. H$_2$SO$_4$gave 2-benzoylpropionamide (48%) and benzil (87%). Photolysis (>280 nm) in acetonitrile, thermolysis in boiling cumene and LiAlH$_4$ reduction gave **2** (47%, almost quantitatively and 82% respectively).

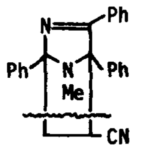
7a; mp. 158-162°; ν_{max}^{Nujol} 2230 cm^{-1} (C≡N); λ_{max}^{EtOH} 222 nm (sh., ε 18300), 266 nm (2450)[13)];

τ^{CDCl_3} 2.03-3.13 (15H, m, aromatic H), 5.97-7.16 (3H, ABC pattern, J_{AB}=12Hz, J_{BC}=5Hz, J_{AC}=10Hz, $-CH_AH_B-CH_C-$), 7.33 (3H, s, $-N-CH_3$); M/e 363 (M^+, rel. int. 0.1), 310 ($[M-CH_2CHCN]^+$, 100). Thermolysis in boiling cumene gave **6** (69%).

7b; mp. 197-200°; ν_{max}^{Nujol} 2230 cm^{-1} (C≡N); λ_{max}^{EtOH} 222 nm (sh., ε 16800), 266 nm (3030)[13]; τ^{CDCl_3} 2.20-3.23 (15H, m, aromatic H), 6.05-6.86 (3H, ABC pattern similar to that of **7a**), 7.40 (3H, s, $-N-CH_3$); M/e 363 (M^+, rel. int. 0.5), 310 ($[M-CH_2CHCN]^+$, 100).

REFERENCES

1. Photoinduced Reactions. LXXIV. Part LXXIII: I. Saito, M. Takami, T. Konoike and T. Matsuura, Bull. Chem. Soc. Japan, 46, 3198 (1973).
2. a) J. J. McCullough and C. W. Huang, Can. J. Chem., 47, 757 (1969); b) R. M. Bowman, T. R. Chamberlain, C. W. Huang and J. J. McCullough, J. Amer. Chem. Soc., 92, 4106 (1970); c) R. M. Bowman and J. J. McCullough, Chem. Comm., 948 (1970); d) B. F. Plummer and R. A. Hall, Chem. Comm., 44 (1970); and references cited therein.
3. a) C. Helene and F. Brum, Photochem. Photobiol., 11, 77 (1970); b) J. L. Fourrey, P. Jouin and J. Moron, Tetrahedron Letters, 3229 (1973).
4. For the photochemical addition of alkenes to heteroaromatics, see a review, S. T. Reid, Adv. Heterocycl. Chem., 11, 1 (1970).
5. It was reported that the thermal reaction of imidazole and acrylonitrile resulted in β-cyanoethylation at position 1. [N. Sawa and S. Okamura, Nippon Kagaku Zasshi, 90, 704 (1969); F. Yamada and Y. Fujimoto, Bull. Chem. Soc. Japan, 44, 557 (1971).]
6. J. Nyitrai and K. Lampert, Tetrahedron, 25, 4265 (1969).
7. The remarkable solvent effect on the photochemical reaction of **6** is under investigation.
8. F. W. Billmeyer, Jr., "Textbook of Polymer Science", John Wiley and Sons., p.292 (1962).
9. N. J. Rose and R. S. Drago, J. Am. Chem. Soc., 81, 6138 (1959).
10. A similar behavior was observed with **6** (isosbestic points: 293 and 261 nm).
11. These protons appear as a doublet because of non-equivalency due to the asymmetric α-cyanoethyl group.
12. The absorption spectrum is similar to that of 2,2-dimethyl-4,5-diphenyl-2H-imidazole; λ_{max}^{EtOH} 262 nm (ε 9700). [D. R. Arnold, V. Y. Abraitys and D. McLeod, Jr., Can. J. Chem., 49, 923 (1971).]
13. These spectral data are consistent with the N-substituted 2-phenyl-2-imidazoline structures but not the Schiff base structure (**i**). 1-Methyl-2-phenyl-2-imidazoline; λ_{max}^{EtOH} 223 nm (ε 9350), 264 nm (ε 2540) [T. Matsuura, Y. Ito and I Saito, Bull. Chem. Soc. Japan, in press]. N-Benzylidenebenzylamine; λ_{max}^{EtOH} 250 nm (ε 20800), 280 nm (sh., ε 2080) [J. P. Phillips and F. C. Nachod (Ed.), "Organic Electronic Spectral Data", Interscience Publ., New York·London (1963), p. 506].



(**i**)