

PHOTOCHEMICAL CONVERSION OF PYRAZOLES TO ENAMINONITRILES AND IMIDAZOLES

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Irradiation of pyrazole, 1-methylpyrazole and 4-cyano-1-methylpyrazole gave 3-aminoacrylonitrile, 3-methylaminoacrylonitrile and 2-cyano-3-methylaminoacrylonitrile along with corresponding imidazoles. A new pathway is proposed in which both enaminonitrile and imidazole are produced immediately from pyrazole, besides the sequence of pyrazole \rightarrow enaminonitrile \rightarrow imidazole.

Schmidt and his coworkers¹⁾ found that some N-alkylindazoles without substituent in the 3-position were converted to 2-aminobenzonitriles. On the other hand, Ferris and his coworkers²⁾ have discovered many examples of the photochemical conversion of enaminonitriles to imidazoles. No conversion of pyrazoles to enaminonitriles is known up to this date.³⁾

We have found that some pyrazoles with hydrogen in the 3-position, such as pyrazole, 1-methylpyrazole and 4-cyano-1-methylpyrazole rearrange photochemically to 3-aminoacrylonitrile, 3-methylaminoacrylonitrile and 2-cyano-3-methylaminoacrylonitrile respectively along with corresponding imidazoles. The reaction was carried out by irradiation with mercury lamp at ordinary temperature in solvent without any sensitizer. The smooth conversion of pyrazoles to enaminonitriles with clean isosbestic points was generally observed when the UV spectrum of the reaction mixture was monitored at intervals of a few minutes (Fig.1).

Fig.1. Photochemical conversion of pyrazoles to enaminonitriles. Pyrazoles irradiated in cell for UV measurement in solvent by lamp with principal emission at 365nm. UV spectral measurements were made at one or two minutes intervals.

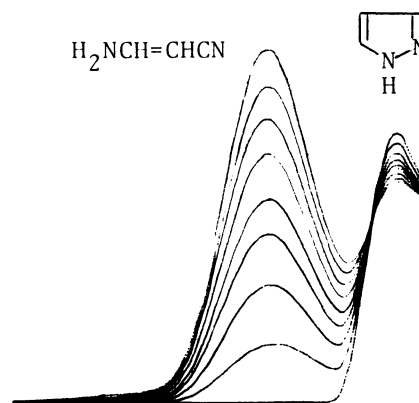


Fig.1a. Pyrazole (UVmax 209nm) to 3-aminoacrylonitrile (UVmax 250nm) in EtOH.

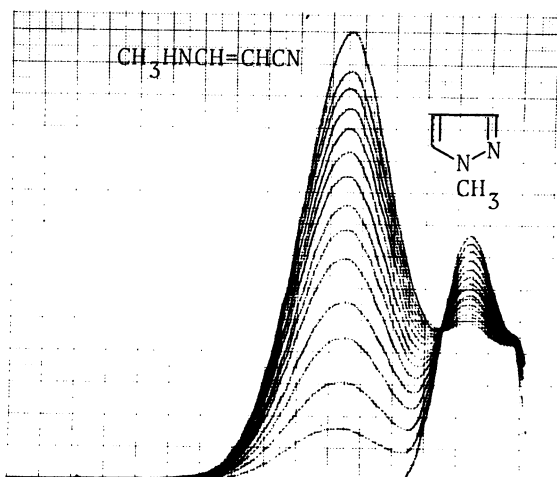


Fig.1b. 1-Methylpyrazole(UVmax 214nm) to 3-methylaminoacrylonitrile(UVmax 255nm) in EtOH.

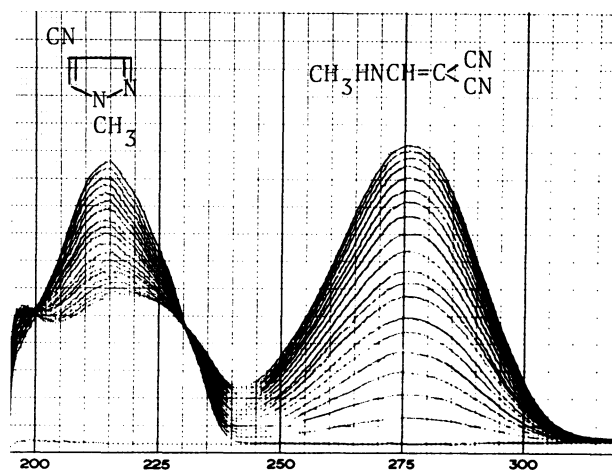


Fig.1c. 4-Cyano-1-methylpyrazole (UVmax 215nm) to 2-cyano-3-methylaminoacrylonitrile(UVmax 277nm) in MeCN.

Results of the present photochemical conversions are summarized in Table 1.

Table 1. Photochemical conversion of pyrazoles to enaminonitriles^{a)} and imidazoles.

$\begin{array}{c} \text{X} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{N} \\ \diagup \quad \diagdown \\ \text{R} \end{array}$		mol($\times 10^2$) in MeCN	Irradiation time(h) ^{a)}	Yield(%) ^{b)}		Pyrazole unchanged
R	X			$\text{RHNCH}=\text{C} \begin{array}{l} \diagup \text{X} \\ \diagdown \text{CN} \end{array}$	$\begin{array}{c} \text{X} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{N} \\ \diagup \quad \diagdown \\ \text{R} \end{array}$	
H	H	1.38	1	13 ^{c)}	2 ^{c)}	45
CH ₃	H	1.38	1	16 ^{d)}	17 ^{c)}	e)
CH ₃	CN	1.66	2.5	32 ^{f)}	38 ^{g)}	4

a) Ushio 100W medium pressure mercury lamp (with principal emission at 365nm) was immersed in MeCN solution of pyrazole. Hanovia 90W lamp was used in the run of R=CH₃ X=CN. b) Generally calculated by GC except for the run of R=CH₃ X=CN in which yield was determined by the amount isolated. c) Identical with an authentic sample.⁴⁾ d) New compound, UVmax 255nm(EtOH) (ϵ 15,000); IR(CHCl₃), 3475(NH), 3010(CH), 2202(CN), 1632(C=C); ¹H-NMR (CDCl₃), δ 2.72(3H,CH₃), 3.90(1H,H-2), 7.06(1H,H-3), J_{H-NH}7.2Hz, J_{H(2)-H(3)}13.7Hz, J_{NH-CH₃}5.0Hz. e) Undetermined. f) Melted at 195-196°C, identical with an authentic sample.⁵⁾ g) Melted at 72-73°C, identical in UV, IR and ¹H-NMR with descriptions in literature.⁶⁾

It is well known that enaminonitriles are converted into imidazoles on irradiation.²⁾ During the present work, 2-cyano-3-methylaminoacrylonitrile was successfully photoisomerized to 4-cyano-1-methylimidazole.⁷⁾

On the other hand, by monitoring the reaction mixture derived from 4-cyano-1-methylpyrazole at short time irradiation intervals, it was seen that 4-cyano-1-methylimidazole was formed as well as 2-cyano-3-methylaminoacrylonitrile even at the beginning of the irradiation, in spite of the much slower conversion of the enaminonitrile to the imidazole under the same irradiation conditions(Fig.2).

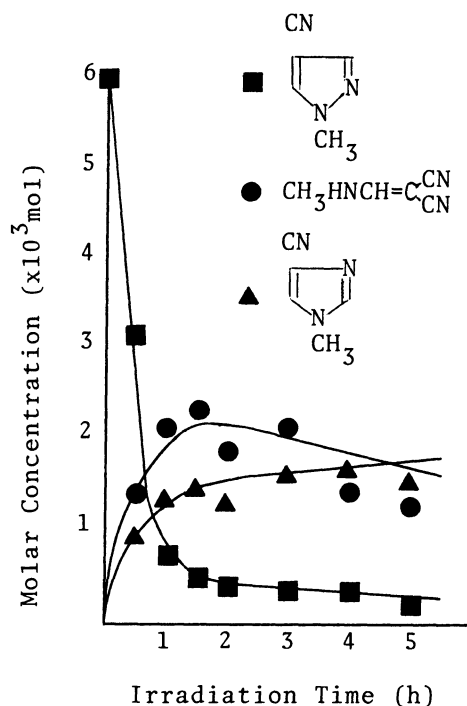


Fig. 2a. Irradiation of 4-cyano-1-methylpyrazole to 2-cyano-3-methylaminoacrylonitrile and 4-cyano-1-methylimidazole.

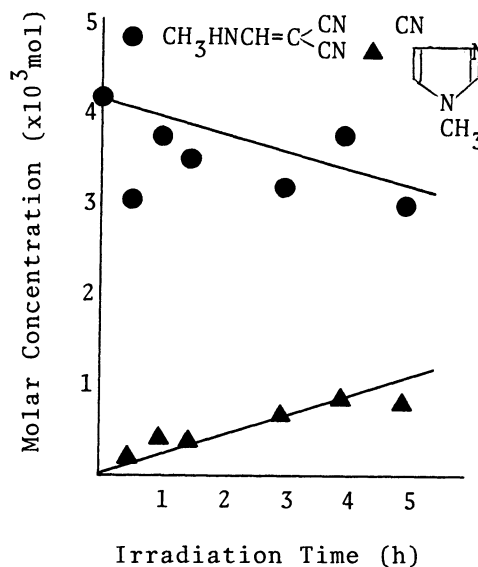


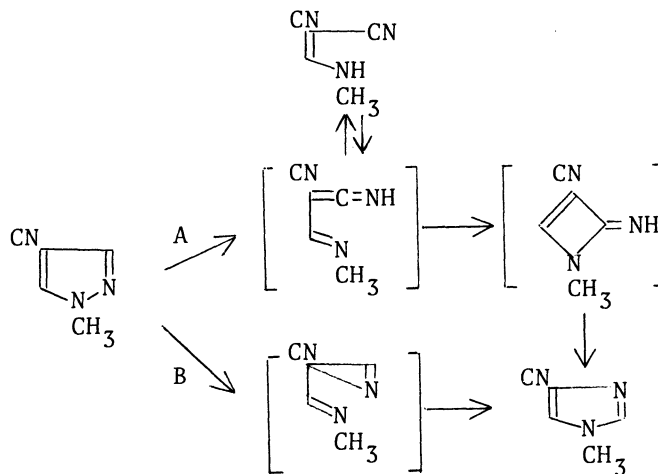
Fig. 2b. Irradiation of 2-cyano-3-methylaminoacrylonitrile to 4-cyano-1-methylimidazole.

Fig. 2. Irradiations of 4-cyano-1-methylpyrazole(2a) and 2-cyano-3-methylaminoacrylonitrile(2b) in MeCN with Ushio 100W medium pressure mercury lamp. Reaction mixture was analyzed by GC at a half hour intervals.

So we have proved that both enaminonitrile and imidazole are produced directly from pyrazole, even though a part of the imidazole is produced indirectly by the sequence of pyrazole \rightarrow enaminonitrile \rightarrow imidazole.

We propose that the reaction mechanism of the present photochemical conversion follows two pathways A and B. Pathway A will involve a ketenimine structure which may rearrange to enaminonitrile and also to imidazole possibly via an iminoazetine intermediate.⁸⁾ Pathway B will be analogous to the photochemical rearrangement of isoxazoles to oxazoles.⁹⁾

Details will be reported later.



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- 2) J. P. Ferris, R. S. Narang, T. A. Newton, and V. R. Rao, *J. Org. Chem.*, 44, 1273 (1979) and references cited therein.
- 3) Recently Grimshaw et al. (*J. Chem. Soc. Perkin I*, 1977, 2096) reported that irradiation of 1,4,5-triphenylpyrazole in the presence of benzophenone gave 3-anilino-2,3-diphenylacrylonitrile (6%), which was itself inert towards irradiation.
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- 7) For example, irradiation of 2-cyano-3-methylaminoacrylonitrile (0.83×10^{-2} mol) in MeCN for ten hours with Hanovia 90W medium pressure mercury lamp gave 4-cyano-1-methylimidazole (39% yield), and 42% of the enaminonitrile was recovered unchanged.
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