Tetrahedron Letters,Vol.23,No.46,pp 4839-4842,1982 0040-4039/82/464839-04$03.00/0
Printed in Great Britain

THE MATRIX PHOTOLYSIS OF PYRIDINE-2,3- AND -3,4-DICARBOXYLIC ANHYDRIDES

Ian R. Dunkin* and J. Gavin MacDonald
Department of Pure and Applied Chemistry, University of Strathclyde,
Cathedral Street, Glasgow, G1 1XL

SUMMARY: Photolysis of anhydrides (1) and (5) in low temperature matrices led to loss of CO and CO_2 in each case, but pyridynes were not detected, and if formed at all, underwent immediate further bond fission.

The discovery that photolysis of maleic anhydride and phthalic anhydride in low-temperature matrices gives acetylene and benzyne, respectively,[1] seemed to promise a convenient general method for producing species with strained triple bonds. Pursuing this idea, we have studied the matrix photolysis of pyridine-2,3- and -3,4-dicarboxylic anhydrides, in the hope of detecting the pyridynes (2) and (6).

Pyridine-2,3-dicarboxylic anhydride (1)[2] was isolated in N_2 matrices by sublimation on to a CsBr window at 20K, with simultaneous deposition of N_2.[3] The temperature was then lowered to 12K. UV-irradiation of the resulting matrix (400 min., 125W medium-pressure Hg arc, with water filter) caused the IR bands of (1) to diminish, while those of CO and CO_2 grew.[4] In addition, several weaker product bands were observed, which can be attributed to <u>cis</u>-β-ethynylacrylonitrile (3) (Table 1). We observed no IR bands that could be attributed to 2,3-pyridyne (2). The anhydride (1) suffers a similar fate during gas-phase pyrolysis, which is reported to give both (3) and its further decomposition products, HCN and butadiyne.[5] The pyridyne (2), therefore, if formed at all, is unstable towards both gas-phase thermolysis and matrix photolysis.

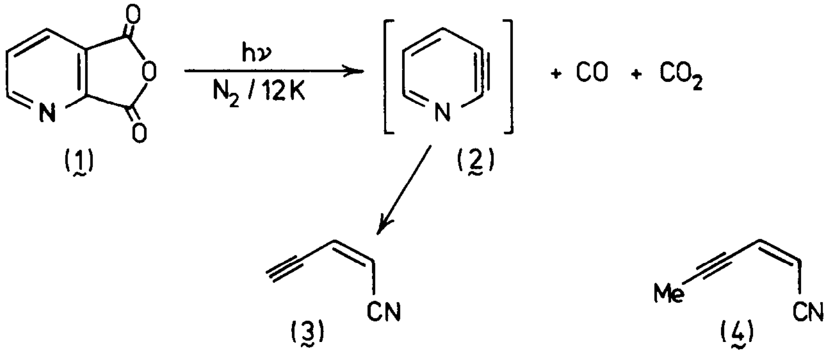

TABLE 1

IR bands (cm^{-1}) of the matrix photoproduct of (1) compared with published IR spectra of (3) and (4).

Photoproduct of (1) in N_2 at 12K.[a]	(3)[b]	(4)[c]	Assignment
3312	3311	-	ν(CH)
2260	2268	2290	ν(C≡C)
2235	2222	2235, 2225	ν(C≡N)
1600	Not reported	1610	ν(C=C)
754	Not reported	Not reported	δ(C≡C-H)

[a] Ref.4 [b] Ref.5 [c] Ref.6

By means of the same sublimation technique used with (1), pyridine-3,4-dicarboxylic anhydride (5)[7] was isolated in both N_2 and Ar at 12K. UV-irradiation (300-400 min.) of the resulting matrices led to decomposition of (5) and the formation of several products, IR bands of which are given in Table 2. All the observed product bands can be attributed satisfactorily to CO, CO_2, HCN, acetylene, or butadiyne. We observed no bands attributable to 3,4-pyridyne (6). The bands due to acetylene were comparatively weak, indicating that fragmentation of (5) in this way is a minor pathway. IR bands due to cyanoacetylene, which presumably accompanies acetylene in this decomposition mode, were not observed in our experiments. No previous study of the photolysis or thermolysis of (5) seems to have been reported. 3,4-Pyridyne (6) has, however, been generated by gas-phase pyrolysis or flash photolysis of pyridine-3-diazonium-4-carboxylate, and was found both to dimerize and to fragment into butadiyne, HCN, acetylene and cyanoacetylene.[8]

Thus for anhydrides (1) and (5), matrix photolysis very probably generates the corresponding pyridynes, but these are unstable and immediately decompose to acyclic products.

We thank the SERC for supporting this work with a Research Studentship (J.G.MacD.) and an equipment grant (I.R.D.).

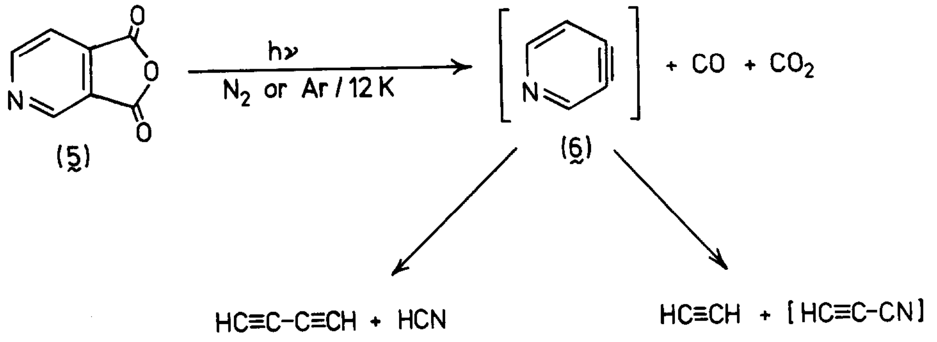

TABLE 2

IR bands (cm^{-1}) of matrix photoproducts of (5) compared with those of authentic compounds.

N_2 at 12K[a]	Ar at 12K[a]	Attribution	Authentic compounds[b]
3314	3320	$HC\equiv CC\equiv CH$	3328
3295	3298	$HC\equiv CC\equiv CH$	3293
3286	3270	HCN	3288
3262	3261	$HC\equiv CH$	3264
2348	2348	CO_2	2348
2184	2184	$HC\equiv CC\equiv CH$	2184
2142	2142	CO	2142
2102	2100	HCN	2097
753	750	$HC\equiv CH$	750
744	743	HCN	746
662	662	CO_2	662
636	636	$HC\equiv CC\equiv CH$	630

[a] Ref. 4

[b] Frequencies for butadiyne are for the gas phase (ref. 9). Others are for N_2 matrices: HCN (ref.10); CO, CO_2 and acetylene (ref. 4).

REFERENCES

1. I. R. Dunkin, and J. G. MacDonald, J. Chem. Soc., Chem. Commun., (1979) 772.
2. Anhydride (1) was a commercial sample (Aldrich) purified further by vacuum sublimation.
3. Cooling was achieved by means of an Air Products Displex, model CSA-202. Matrix gases were from BOC Ltd., research grade. Owing to the sublimation technique used for matrix deposition, matrix ratios could not be estimated.
4. IR spectra were recorded on a JASCO IRA-2 spectrometer and are accurate ± 8 cm^{-1} (above 2000 cm^{-1}) or ± 4 cm^{-1} (below 2000 cm^{-1}). IR bands of CO, CO_2 and acetylene were compared in our own laboratory with those of authentic samples in N_2 at 12K.
5. M. P. Cava, M. J. Mitchell, D. C. De Jongh, and R. Y. Van Fossen, Tetrahedron Lett., (1966) 2947.

6. K. G. Golodova, S. I. Yakimovich, and F. Ya. Perveev, *J. Org. Chem., USSR*, **8**, 2292 (1972).

7 (a) Anhydride (**5**), m.p. 77-78°, was prepared in high yield by sublimation (160°/0.5 torr) of the commercially available pyridine-3,4-dicarboxylic acid (Aldrich).

(b) B. Fels, *Ber.*, **37**, 2129 (1904).

8. J. Kramer, and R. S. Berry, *J. Am. Chem. Soc.*, **94**, 8336 (1972).

9. I. Freund, and R. S. Halford, *J. Chem. Phys.*, **42**, 4131 (1965).

10. C. M. King, and E. R. Nixon, *J. Chem. Phys.*, **48**, 1685 (1968).

(Received in UK 23 August 1982)