Photochemical Transformations of 3,3,4,7-Tetramethylpyrazolo[3,4-*d*]pyridazine in Solution and Frozen Gas Matrices

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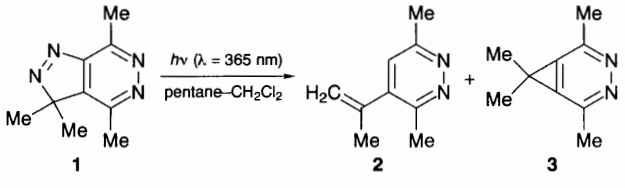
Photochemical transformations of pyrazolopyridazine **1** give isopropenylpyridazine **2** in addition to cyclopropapyridazine **3** in solution and to the ring-opened diazo isomer **4** observed in frozen gas matrices.

Photochemical cycloelimination of nitrogen from cyclic azo compounds has attracted considerable interest from both mechanistic and synthetic viewpoints.[1] Cyclopropabenzene[2] and cyclopropapyridine[3] have successfully been generated by this approach.

In this communication photochemical transformations of 3,3,4,7-tetramethylpyrazolo[3,4-*d*]pyridazine **1**† are discussed. The study was aimed at characterization of reactive intermediates intercepted in solution and cryogenic gas matrices.

Irradiation of **1** in pentane–CH_2Cl_2 (9 : 1, *v*/*v*) at 5 °C with a high-pressure mercury lamp through a 365 nm filter gave a mixture of products which were separated by preparative TLC and characterized by NMR spectroscopy (Scheme 1).‡ All operations concerning separation and isolation of the products were performed below 10 °C. The relative ratio of 3,6-dimethyl-4-isopropenylpyridazine **2** to 1,4,7,7-tetramethylcyclopropa[*d*]pyridazine **3** present in the reaction mixture was found to be a function of irradiation time as shown in Fig. 1. The previously unobserved cyclopropapyridazine **3** was found to be unstable at the temperature of irradiation and isomerized quantitatively to olefin **2** in a few hours.

In contrast, irradiation of **1** in nitrogen and argon matrices at 10 K did not lead to complete cycloelimination of nitrogen.§



Scheme 1

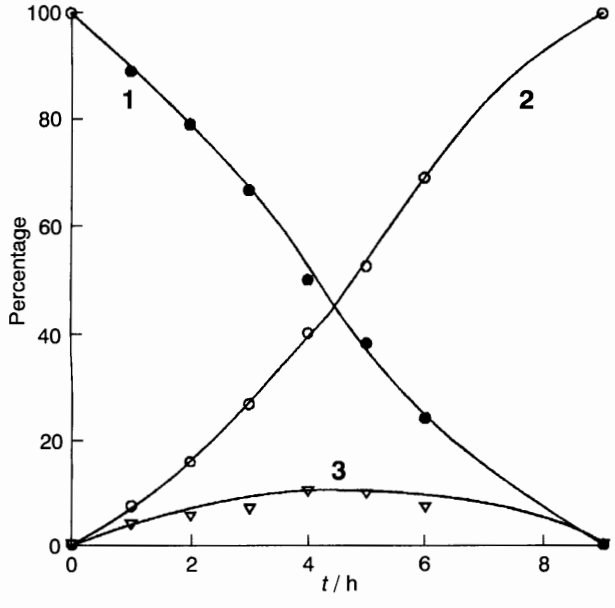


Fig. 1 Composition of the reaction mixture as a function of irradiation time

Along with olefin **2**¶ formation of the ring-opened diazo isomer **4**, generated from **1** by cleavage of the single bond in the azo function of the five-membered ring, seems to be evident (Scheme 2).‖ Changes observed in the representative region of the IR spectrum are shown in Fig. 2. A characteristic stretching vibration of the diazo function observed at 2052 cm^{-1} along with the weak, broad and structureless electronic absorption with λ_{max} = 510 nm support the assignment of **4**.

The diazo isomer **4** can be converted to olefin **2** by irradiation with visible light. No evidence for stabilization of carbene **5** in either nitrogen or argon matrices was found, most likely due to the fast 1,4-hydrogen atom transfer leading to **2**. Fast 1,4-hydrogen atom transfer in carbenes in cryogenic matrices with an involvement of quantum-mechanical tunnelling has already been observed.[5,6]

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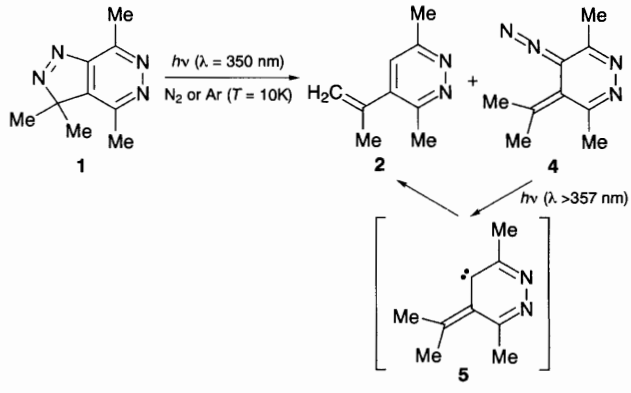

Scheme 2

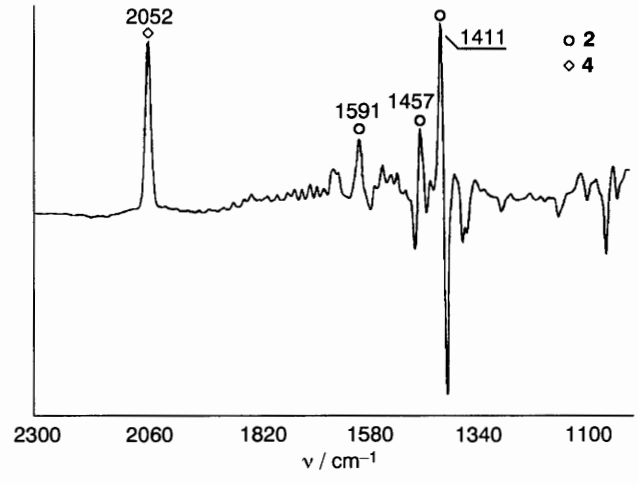

Fig. 2 Difference IR spectrum of 3,3,4,7-tetramethylpyrazolo[3,4-*d*]pyridazine isolated in nitrogen matrix at 10 K obtained by subtraction of the spectrum recorded before irradiation from the spectrum recorded after irradiation for 90 min through a 350 nm interference filter

Professor M. Franck-Neumann for the sample of pyrazolopyridazine.

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Footnotes

† Compound **1** was prepared from 4,5-diacetyl-2,3-dimethyl-3*H*-pyrazole and hydrazine hydrate by M. Franck-Neumann (Université Louis Pasteur, Strasbourg, France), unpublished work.

‡ *Selected spectroscopic data.* ^{1}H NMR (200 MHz, $CDCl_3$, *T* 263 K) **2**: 7.00 (s, 1H, H-5), 5.33 and 5.00 (2H, CH_2=C), 2.66 (s, 6H, Me C-3 and Me C-6), 2.05 (3H, Me–C=C). **3**: 2.77 (s, 6H, Me C-2 and Me C-5), 1.66 (s, 6H, 2 Me C-7).

§ Experimental details of matrix isolation experiments are given elsewhere.[4]

¶ Relative intensities and positions of vibrational bands assigned to **2** were identical with those observed in IR spectrum recorded for the authentic sample under matrix isolation condition.

‖ No evidence for the formation of **3** was found upon photolysis of matrix-isolated **1**.

References

1 H. Meier and K.-P. Zeller, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 835.
2 R. Anet and F. A. L. Anet, *J. Am. Chem. Soc.*, 1964, **86**, 525.
3 R. Bambal, H. Fritz, G. Rihs, T. Tschamber and J. Streith, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 668.
4 S. Kuberski and J. Gebicki, *J. Mol. Struct.*, 1992, **275**, 105.
5 R. J. McMahon and O. L. Chapman, *J. Am. Chem. Soc.*, 1987, **109**, 683.
6 J. Gebicki and S. Kuberski, unpublished work.