Photolysis of *N*-Ethoxycarbonyliminopyrazinium Ylides: Formation of Pyrazoles

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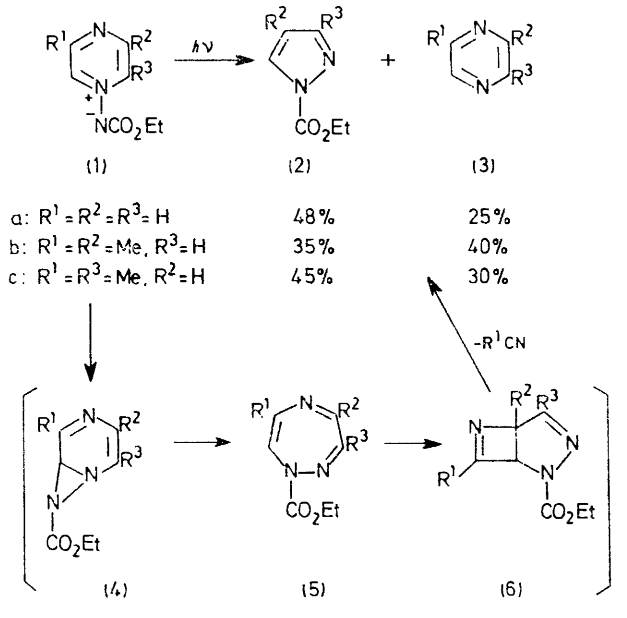
Summary Photolysis of the *N*-ethoxycarbonyliminopyrazinium ylides (**1**) affords pyrazoles (**2**), probably *via* 1,2,5-triazepine intermediates (**5**).

IN connection with the photochemistry of various types of aza-aromatic *N*-ylides such as pyridinium,[1,2] quinolinium[3,4] and benzocinnolinium[5] *N*-ylides, it seemed of general interest to examine the photochemical behaviour of diaza-aromatic *N*-ylides. We now report our results on the photolysis of the *N*-iminopyrazinium ylides (**1**).

Irradiation (100 W, high-pressure Hg lamp; Pyrex) of the ylides (**1**)† for 7—8 h in acetone solution and chromatography over silica gel gave the 1-ethoxycarbonylpyrazoles (**2**)‡ and the parent pyrazines (**3**) in the yields shown in the Scheme. Besides these products, HCN (from **1a**) and MeCN (from **1b**,**c**) were also formed.

Several types of photochemical reaction of *N*-substituted *N*-imines have been observed, mainly in the pyridine[1] and quinoline[3] series; *i.e.*, (i) ring expansion to 1,2-diazepines, (ii) rearrangement to 2-amino-derivatives, and (iii) N–N bond fission to the parent amines.



SCHEME

Although all attempts to isolate the intermediates (**5**) and (**6**) failed, we believe that a reasonable mechanism for the formation of the pyrazoles (**2**) involves initial ring expansion to the 1,2,5-triazepines (**5**)§ *via* the diaziridine inter-

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† The ylides (**1**) were prepared by *N*-amination of the pyrazines with *O*-mesitylenesulphonylhydroxylamine by the method of Y. Tamura, J. Minamikawa, K. Sumoto, S. Fujii, and M. Ikeda, *J. Org. Chem.*, 1973, **38**, 1239. Structure elucidation is based on spectral data and elemental analysis; *e.g.* (**1a**): m.p. 92—93 °C; δ ($CDCl_3$) 9·14—9·24 (2H, m), 8·66—8·76 (2H, m), 4·18 (2H, q), and 1·32 (3H, t).

‡ The pyrazole (**2a**) was characterized by comparison with an authentic sample prepared from pyrazole and ethyl chloroformate in tetrahydrofuran; (**2a**): oil, ν (liq.) 1760 cm^{-1}; δ ($CDCl_3$) 6·40 (1H, dd), 7·72 (1H, d), 8·14 (1H, d), 4·50 (1H, d), and 1·45 (3H, t). The other pyrazoles (**2b**,**c**) were characterized by spectral comparison with (**2a**) and elemental analysis.

§ To our knowledge, monocyclic 1,2,5-triazepine derivatives have not yet been reported.

mediates (4) by analogy with *N*-iminopyridinium ylides.[1] The triazepines (**5**) may then isomerize to the bicyclic valence isomers (**6**), followed by extrusion of R^1CN to produce the pyrazoles (**2**); 1,2,4-triazepines undergo rapid and quantitative thermal conversion into pyrazoles with loss of nitriles.[6]

The orientation of the methyl group in (**2c**) was established by its n.m.r. spectrum. The cyclization of the unsymmetrical ylide (**1c**) to the diaziridine intermediate (**4c**) takes place preferentially at the unsubstituted α-position, by analogy with the case of 2-substituted pyridines.[1]

In the present reaction, rearrangement to 2-aminopyrazines was not observed.

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