

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

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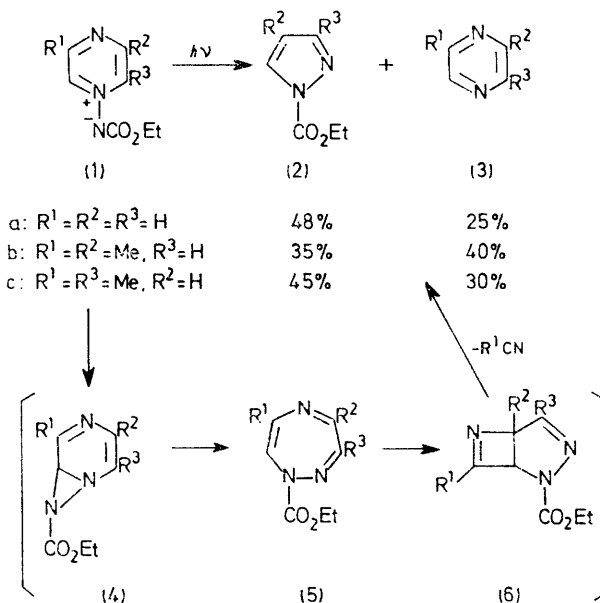
Summary Photolysis of the *N*-ethoxycarbonyliminopyrazinium ylides (1) affords pyrazoles (2), probably via 1,2,5-triazepine intermediates (5).

In connection with the photochemistry of various types of aza-aromatic *N*-ylides such as pyridinium,^{1,2} quinolinium^{3,4} and benzocinnolinium⁵ *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 pyridine¹ and quinoline³ 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.

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-



SCHEME

[†] 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 (CDCl₃) 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 (CDCl₃) 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 R¹CN 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 un-

symmetrical 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-amino-pyrazines was not observed.

(Received, 2nd February 1976; Com. 108.)

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