The Photolysis of *N*-Acyliminopyridinium Ylides[1]

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Summary Photolysis of the pyridinium ylides (**2**) results in ring expansion to diazepines (**2**) and fragmentation to pyridines (**4**) and methyl isocyanate.

RECENT work[2,3] concerning the photochemistry of *N*-ethoxycarbonyliminopyridinium ylides, *e.g.*, (**1**) prompts me to report different preliminary observations in the photochemical behaviour of the analogous *N*-acetyl derivatives (**3**), fragmentation to pyridines (**4**) and methyl isocyanate. The latter, a result of photochemical Curtius rearrangement,[5] was trapped in each case with aniline as *N*-methyl-*N'*-phenylurea. The results are summarised in the Table. The spectral data of the diazepines (**3**), in particular their n.m.r., are in agreement with the suggested structures and may be compared with those reported[2,3] for the related diazepines obtained from the photolysis of the derivatives (**2a**—**c**). Irradiation of ylides (**2**)[4] in methylene chloride at 10—20° in a Pyrex vessel using a Rayonet reactor gave, besides ring expansion to the 1*H*-1,2-diazepine ylides (**1**).[6] It may be noted that in the case of (**2b**), a 2-methyl substituent does not appreciably affect the amount of fragmentation but does direct rearrangement exclusively to yield the diazepine (**3**), $R^1 = Me$, $R^2 = H$ and not the isomeric (**3**), $R^1 = H$, $R^2 = Me$. On the other hand, the ylide (**2c**) undergoes substantially more fragmentation as might be expected from the greater hindrance to ring expansion presented by the 2,6-dimethyl substitution.

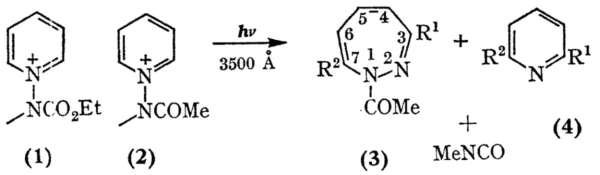
TABLE

Ylide	Diazepine[a]	yield	n.m.r.[b]	Pyridine[c]	yield
(**2**) **a**	(**3**) **a**	55%	7·75 (s, 3H, $COCH_3$), 4·22 and 3·60 (m, 4H, 4-H, 7-H), 2·65 (br d, 1H, *J* 2·5 Hz., 3-H).	(**4**) **a**	37%
b	**b**	60	7·92 (s, 3H, 3-Me), 7·82 (s, 3H, $COCH_3$), 4·30 and 3·58 (m 4H, 4-H, 7-H).	**b**	33
c	**c**	38	7·88 (s, 3H, 7-Me), 7·85 (s, 3H, 3-Me), 7·80 (s, 3H, $COCH_3$), 4·08 and 3·62 (m, 3H, 4-H, 6-H).	**c**	62

[a] All new compounds gave satisfactory elemental analyses and showed similar i.r. and u.v. spectra *e.g.*, (**3a**): ν (neat) 1668 cm.$^{-1}$ (C=O) and λ_{max} (MeOH) 217 (10,020), 265 sh (4660) nm.

[b] Obtained in $CDCl_3$ solution and expressed in τ values downfield from internal Me_4Si.

[c] Isolated as picrate derivatives.



(**a**) $R^1=R^2=H$; (**b**) $R^1=Me$, $R^2=H$; (**c**) $R^1=R^2=Me$

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[2] J. Streith and J. M. Cassal, *Angew. Chem. Internat. Edn.*, 1968, **7**, 129; J. Streith and J. M. Cassal, *Tetrahedron Letters*, 1968, **4541**.

[3] T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Comm.*, 1969, 432.

[4] T. Okamoto, M. Hirobe, and H. Ohsawa, *Chem. Pharm. Bull. Japan*, 1966, **14**, 518.

[5] Thermal equivalents of this reaction are known: S. Wawzonek and R. C. Gueldner, *J. Org. Chem.*, 1965, **30**, 3031.

[6] For our work with ylides (**1**), see: V. Snieckus, J. M. McIntosh, and A. Balasubramanian, *Canad. J. Chem.*, submitted for publication.