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REGIOSPECIFIC VERSUS NON-REGIOSPECIFIC PHOTOINDUCED RING-ENLARGEMENT OF 3-SUBSTITUTED 1-IMINOPYRIDINIUM YLIDES

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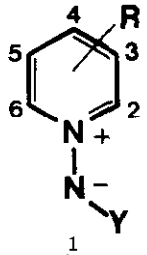
The photoinduced ring enlargement of 1-iminopyridinium ylides 1, leading to the isomeric 1,2-diazepines 3, is by now a well established ring transformation (1), although the scope and limitations of this rearrangement have not been investigated thoroughly as yet. Along these lines we investigated the effect of substituents attached to carbon atom C-3 of the pyridinium ylides on the ring enlargement process. In the absence of any regiospecificity two isomers would be expected to form photochemically from such ylides, namely 4- and 6-substituted diazepines. Conversely, C-3 substituents having a strong electronic directing effect in the excited state could lead regiospecifically to only one diazepine. It should be noted that contrary to some observations we have made during the photochemistry of C-2 substituted pyridinium ylides (2), steric effects should not play any role in the photoinduced ring expansion process of C-3 substituted 1-iminopyridinium ylides. In order to account for the photoinduced ring enlargement, 1,7-diazanorcaradienes 2 have been postulated as intermediates along the reaction pathway leading from the ylides 1 to the corresponding 1,2-diazepines 3 (3,4,5). Although such bicyclic compounds have not been detected yet, we assume their occurrence for operational purposes.



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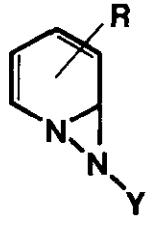

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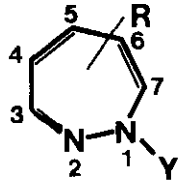
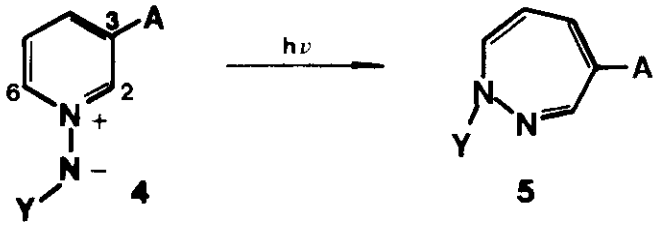


3

Electron attracting substituents by virtue of a mesomeric effect showed a remarkable directing effect upon the photoinduced ring enlargement. UV irradiation of the ylides 4a-c leads in high chemical yield to only 4-substituted 1,2-diazepines 5a-c (Table 1) (7). In a typical example a solution of 1g 3-cyano-benzoylimino-pyridinium ylide 4b in 500 ml benzene was irradiated through Pyrex glass by means of a 125 Watt Hg high pressure lamp. After 15 hours all starting material was consumed, the solvent was removed and the residue was crystallized

from cyclohexane. 1-Benzoyl-4-cyano-1,2-diazepine 5b, m.p.165-166°, was obtained in 84% yield as orange crystals: [IR (KBr disc) ν (C≡N) 2240, ν (C=O) 1645; NMR ($CDCl_3$) δ 6.05 (H-6; q; $J_{6,7}$=7.5 and $J_{6,5}$=5.5Hz), 6.90 (H-7; d; $J_{7,6}$=7.5Hz) and 7.5 ppm (H-3, H-5 and 5 arom.protons, m)]. No other diazepines could be detected.



a) A = Y = CO_2Et b) A = CN; Y = COPh c) A = $CONH_2$; Y = COPh

According to previous measurements and calculations (9) π-π^* transitions are thought to be responsible for the photoinduced ring enlargement process of 1-iminopyridinium ylides 1. On the other hand all ylides show a strong negative solvatochromism (10) which points to an intramolecular charge transfer process. Recent EHMO calculations performed with model 4 (A=CN; Y=H) predict a regiospecific ring enlargement and agree with our experimental results (Table 1) provided that a $\pi_1^1 \rightarrow \pi_{-2}^1$ transition is postulated (11).

Table 1 1,2-Diazepines 5 obtained by UV irradiation from ylides 4 by a regiospecific ring enlargement process.

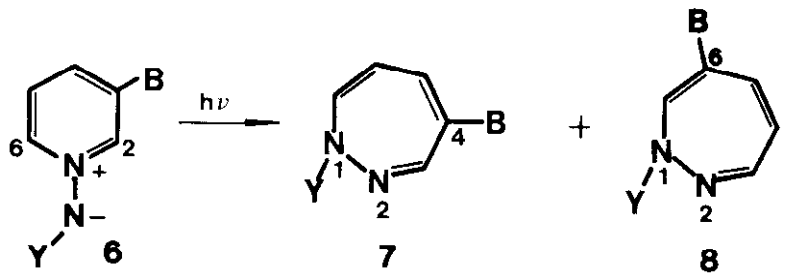
	yield %	mp	UV (MeOH) λ_{max} (ε)	^{1}H NMR of H-5 δppm (J_{56}Hz)
5a	80(6)	oil	222 nm (9700) 300 nm (900)	7.37 (6.0)
5b	84	165-166°	232 nm (8000) 360 nm (500)	7.5 (5.5)
5c	86	80-85°	229 nm (17000) 370 nm (2200)	7.5 (6.0)

In contrast to electron-attracting substituents, electron-donating groups (mesomeric and hyperconjugative) at the 3-position showed little orienting effect on the photoinduced ring expansion process. Two photoisomers were obtained in high yield: 4-substituted diazepines 7, and 6-substituted diazepines 8 (Table 2). With the exception of methyl substituted compounds 7a and 8a, all diazepines described in Table 2 are crystalline products (12).

In a typical example ylide 6e (1.0g), which was synthesized according to Tamura's procedure(8) was irradiated in benzene (500 ml) through Pyrex glass by means of a Hg high pressure lamp for 10 hours. After removal of the solvent in vacuo, the residue was chromatographed over silicic acid (100 g) with a mixture of cyclohexane and ethyl acetate 9/1 v/v. Two compounds were isolated: 1-benzoyl-4-bromo-1,2-diazepine 7e (560 mg), mp 120-121° [^{1}H-NMR ($CDCl_3$) δ 7.4 (H-3; singlet); 6.9 (H-5, doublet; $J_{6,5}$ 5.5 Hz); 6.5 (H-7; doublet; $J_{7,6}$ 7.5 Hz) and

5.65 ppm (H-6; quadruplet; $J_{7,6}$ 7.5 Hz and $J_{5,6}$ 5.5 Hz)] and 1-benzoyl-6-bromo-1,2-diazepines 8e (240 mg), mp 94-95° [^{1}H NMR ($CDCl_3$) δ 7.4 ppm (H-3; multiplet), 6.7 (H-5; doublet of doublet; $J_{4,5}$ 11 Hz and $J_{5,3}$ 1.2 Hz), 6.7 (H-7; singlet) and 6.3 ppm (H-4; quadruplet; $J_{5,4}$ = 11 Hz and $J_{4,3}$ = 3 Hz)].

As can be seen from Table 2, 4-substituted isomers are obtained in higher yield than 6-substituted ones (13). It would seem therefore that there is a slight directing effect due to the C-3 substituents during photochemical ring expansion of ylides 6. For the time being there is no straightforward explanation for these results.



a) B = Me; Y = CO_2Et
b) B = OCOPh Y = COPh
c) B = F; Y = COPh
d) B = Cl ; Y = COPh
e) B = Br ; Y = COPh
f) B = I ; Y = COPh

Table 2: 1,2-Diazepines 7 and 8 obtained by UV irradiation of ylides 6 by non-regiospecific enlargement.

	chemical yield %	Ratio 7/8	mp	UV (MeOH) λ_{max} nm(ε)
7a	81	1,5	oil	224 (8,500) 350* (260)
8a			oil	224 (8,000) 330* (240)
7b	74	1.86	132-133°	235 (23,000) 350* (570)
8b			143-144°	233 (13,500) 350* (380)
7c	80	1.22	80-81°	227 (8,500) 362 (200)
8c			121-122°	225 (10,500) 360 (250)
7d	75	1.5	120-121°	230 (10,500) 358 (470)
8d			110-111°	227 (13,000) 358 (300)
7e	80	2.33	120-121°	226 (14,200) 358 (400)
8e			94-95°	227 (12,000) 360 (410)
7f	60**	1.86	135-136°	227 (13,500) 363 (690)
8f			116-117°	228 (15,500) 362 (310)

* shoulder

** 4-phenyl-1,2-diazepine is also isolated in 8% yield as a secondary photoproduct.

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7) All the 1-iminopyridinium ylides described here can easily be obtained using Tamura's approach (8): the corresponding pyridines are treated with mesitylsulfonylhydroxylamine (MSH) leading to 1-aminopyridinium salts; acylation of their amino groups followed by base induced deprotonation gives the ylides in good overall yields.

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12) All new compounds gave satisfactory elemental analyses. UV, IR, ^{1}H and ^{13}C NMR spectra fully agree with their proposed structure.

13) We found that ylides 1 (14) which bear OH, NH_2 or NHCOPh substituents in the C-3 position, photoisomerise to the corresponding 2- and 6-amino-pyridines, no 1,2-diazepines being detected. In our opinion a different photoinduced reaction mechanism occurs which does not involve the intermediacy of diazepines.

14) J.L.Schuppiser and J.Streith, unpublished results.