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274. Photochemistry of 3-Substituted 1-Iminopyridinium Ylides[1]). Regiospecific *versus* Non-regiospecific Photoisomerization Patterns [1]

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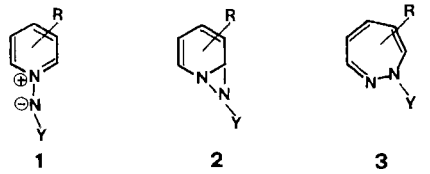
Summary

3-Substituted 1-iminopyridinium ylides **1** undergo photo-induced ring enlargement to 1 *H*-1,2-diazepines. With strongly electron-withdrawing substituents the ring expansion process is regiospecific and leads exclusively to 4-substituted 1 *H*-1,2-diazepines. Weak electron-donating substituents, like a methyl group and halogen atoms, do not have any directing effect since both 4- and 6-substituted 1 *H*-1,2-diazepines are obtained. With strong electron-donating substituents no diazepines are formed; instead one observes photo-induced isomerization to the 2-aminopyridine derivatives, the process being non-regiospecific. Regiospecific photo-induced ring expansion processes are explained in terms of a simple HMO model.

Introduction. – The photo-induced ring enlargement of 1-iminopyridinium ylides **1**, which leads to the isomeric 1 *H*-1,2-diazepines **3**, is a well established ring transformation [2]. The scope and limitation of this rearrangement have not been studied in great detail so far. Therefore, we have investigated directing effects of substituents, attached to C(3) of the ylides **1**, on the ring enlargement process.

[1]) Part 10 of the series 'Photochemical Synthesis of 1,2-Diazepines'. Part 9: [17].
[2]) Basel.
[3]) Darmstadt.
[4]) Mulhouse.

Scheme 1



1 **2** **3**

In the absence of any regiospecificity two isomers should be formed photochemically, namely the 4- and 6-substituted 1 *H*-1,2-diazepines. Conversely, regiospecific ring enlargement would lead either to 4-substituted or to 6-substituted 1 *H*-1,2-diazepine.

We assumed that steric factors play the dominant role [3] in the regiospecific ring expansion of photo-excited 2-substituted *N*-iminopyridinium ylides to the corresponding 3-substituted 1 *H*-1,2-diazepines. With 3-substituted 1-iminopyridinium ylides there is obviously no steric interference between N(1) and C(3) substituents. Therefore, electronic factors were assumed to be mainly responsible for the direction of the ring expansion process.

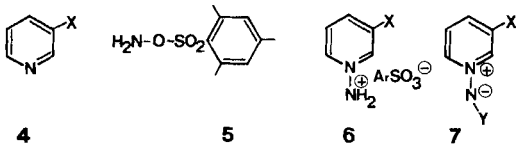
To explain the photochemical formation of 1 *H*-1,2-diazepines we [4] and others [5] have postulated the occurence of the short-lived 1,7-diazanorcaradiene intermediates **2** *(Scheme 1),* although such bicyclic compounds have not been detected so far by any spectroscopic or chemical method.

Nevertheless this mechanistic scheme appears to be a reasonable interpretation for the photo-induced ring expansion since some nonaromatic azomethine imines are known to undergo photoinduced electrocyclic ring closure to the corresponding diaziridines [6] [7]. 1,7-Diazanorcaradienes **2**, the postulated primary photoproducts, would then undergo a concerted thermal disrotatory ring opening [8]. Electronic properties of substituents attached to C(3) of electronically excited ylides **1** should therefore impinge upon the formation of either one of the two possible diazanorcaradienes.

Synthesis of 3-substituted 1-iminopyridinium ylides 1. – Most of the 3-substituted 1-iminopyridinium ylides have been synthesized by treating the appropriate 3-substituted pyridine **4** with mesitylsulfonylhydroxylamine (**5**) [9]. The corresponding *N*-aminopyridinium mesitylsulfonate **6** (Ar = mesityl) treated i) with benzoyl chloride ii) with aqueous sodium hydroxyde, led to the corresponding 1-iminopyridinium ylides **7** (Y = COPh). These are colourless high-melting compounds.

For the synthesis of some 1-iminopyridinium ylides, individual methods had to be used; ylide **7n** was prepared according to the above described general procedure; bis-benzoylation occurred when the 1,3-bisaminopyridinium mesitylsulfonate was treated with benzoyl chloride. Selective hydrolysis of ylide **7n** with aqueous potas-

Scheme 2



4 **5** **6** **7**

Table 1. *Properties of 3-substituted 1-iminopyridinium ylides* **7** *synthesized according to* Tamura et al. [9]

	X[a])	Y[a])	Overall yield [%][b])	m.p. [°C]	UV. (EtOH) λ_{max} (ε) [nm]	IR. (KBr) ν(C=O) [cm^{-1}]
7a	CO_2Et	CO_2Et	48	93	324 (5000)[c])	1640
7b	CN	COPh	48	171–172	346 (5200)	1555
7c	$CONH_2$	COPh	43	265–267	331 (4200)	1700 1550
7d	CH_3	CO_2Et	40	103	336 (8000)[c])	1640
7e	F	COPh	20	181–182	335 (6100)	1560
7f	Cl	COPh	32	150–151	338 (5700)	1550
7g	Br	COPh	39	133–134	337 (6100)	1550
7h	I	COPh	41	106–107	336 (4000)	1540
7i	OCOPh	COPh	58	196–197	330 (5200)	1745 1555
7j	$N<^{CO}_{CO}$	COPh	60	260–265	326 (3900)	1725 1555
7k	Ph	COPh	50	110–120	303 (5500)	1550
7l	OH	COPh	64	240–245	322 (4100)	1530
7m	NMe_2	COPh	55	151–152	355 (4000)	1550
7n	NHCOPh	COPh	45	260–265	324 (5000)	1540
7o	NH_2	COPh	40	205–210	321 (4100)	1550
7p	OCH_3	COPh	28	137–138	322 (6000)	1545

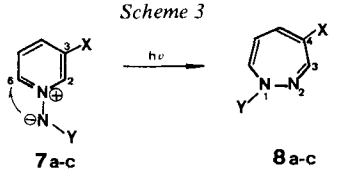
[a]) Explanation *Scheme 3.*
[b]) Calculated with respect to the corresponding pyridines **4**.
[c]) In $CHCl_3$, see [10].

sium hydroxide led to 1-benzoylimino-3-aminopyridinium ylide **7o**. The carbamoyl ylide **7c** was obtained by acid hydrolysis, followed by sodium hydroxide treatment of the corresponding 3-cyano ylide **7b**. The 3-methoxypyridinium ylide **7p** was prepared by diazomethane treatment of the 3-hydroxy ylide **7l**.

Characteristic physical data of these ylides are collected in *Table 1*. The UV. spectra are very similar in shape and show a photoreactive band at λ_{max} 320–340 nm (ε: 4000–6000) in ethanol. Furthermore, the ν(C=O) IR. bands of the *N*-benzoyl groups at 1550 cm^{-1}, are a good indication for their zwitterionic structure.

Photochemistry of 1-iminopyridinium ylides substituted at C(3) with electron-attracting groups: regiospecific ring enlargement. – Electron-attracting substituents by mesomeric effect (X: C=O; C≡N) impose a remarkable regiospecificity upon the photo-induced ring enlargement of the corresponding ylides **7a–c**. UV. irradiation of these compounds led in high chemical yield to the 4-substituted 1*H*-1,2-dia-

Scheme 3



7a-c **8a-c**

Table 2. *Spectroscopic and other data of diazepines* **8a–c**

	Yield [%]	M.p. [°C]	UV. (MeOH) λ_{max}[a]) (ε) [nm]	^{1}H-NMR. ($CDCl_3$) δ(ppm), J(Hz)
8a	80	red oil	300 sh (900) 222 (9700)	H–C(3): 7.7; *d*, $J_{3,5}=1.2$ H–C(5): 7.35; *d*×*d*, $J_{5,6}=6.0$, $J_{5,3}=1.2$ H–C(7): 6.4; *d*, $J_{7,6}=7.5$ H–C(6): 5.7; *d*×*d*, $J_{6,7}=7.5$, $J_{6,5}=6.0$
8b	84	166	360 (470) 272 sh (4900) 232 (8000)	H–C(3), H(5): 7.5; *m*, $J_{5,6}=5.5$ H–C(7): 6.9; *d*, $J_{7,6}=7.5$ H–C(6): 6.05; *d*×*d*, $J_{6,5}=5.5$, $J_{6,7}=7.5$
8c	86	80–85	370 (2200) 270 sh (8500) 229 (17000)	H–C(3): 8.0; *s* H–C(5): 7.4; *m*, $J_{5,6}=6.0$ H–C(7): 6.7; *d*, $J_{7,6}=7.5$ H–C(6): 6.0; *d*×*d*, $J_{6,5}=6.0$, $J_{6,7}=7.5$

[a]) sh = Shoulder.

zepines **8a–c** *(Scheme 3)*, none of the corresponding 6-substituted diazepines having been detected. The structure of these diazepines is easily ascertained by ^{1}H-NMR. spectroscopy *(Table 2)*. In particular, proton H(6), which would be missing if the 6-substituted 1 *H*-1,2-diazepine were formed *(vide infra)* appears as a typical doublet ($J_{7,6}=7.5$ Hz; $J_{6,5}=6$ Hz) at relatively high field ($\delta<6$ ppm). UV. spectra of all 1,2-diazepines described are similar *(Table 2)*. There is always a low intensity, high wavelength band at about λ_{max} 360 nm which accounts for the yellow to orange

Table 3. *UV. spectroscopic and other data of diazepines* **9d–k** *and* **10d–k**

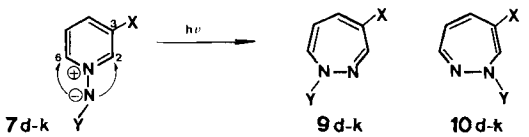
	Yield [%]	Ratio[a]) **9/10**	M.p. [°C]	UV. (MeOH) λ_{max}[b]) [nm] (ε)
9d	81	1.5	oil	350 sh (260); 240 sh (6000); 224 (8500)
10d			oil	330 sh (240); 250
9e	80	1.22	80–81	362 (200); 278 sh (4400); 227 (8500)
10e			121–122	360 (250); 278 sh (4600); 225 (10600)
9f	75	1.5	120–121	358 (460); 272 (6200); 230 (10700)
10f			110–111	358 (310); 272 (6900); 227 (13000)
9g	80	2.33	120–121	358 (400); 286 sh (5600); 226 (14000)
10g			94–95	360 (400); 284 sh (5400); 227 (12000)
9h[c])	52	2.33	135–136	363 (690); 260 (9700); 227 (12500)
10h[c])			116–117	362 (320); 260 (11000); 228 (15500)
9i	74	1.86	132–133	350 sh (570); 273 sh (8000); 235 (23000)
10i			143–144	350 sh (380); 270 sh (6800); 233 (19400)
9j	82	1.22	190–191	350 sh (340); 253 sh (6000); 228 (7500)
10j			176–177	350 sh (300); 260 sh (6400); 225 (11000)
9k	72	1.5	oil	300 sh (7500); 274 (9000); 228 (10000)
10k			oil	370 sh (500); 278 sh (11500); 228 (13000)

[a]) Determined by NMR.
[b]) sh = Shoulder.
[c]) 4-Phenyl-1*H*-1,2-diazepine is also isolated (8%) as a secondary photo-product.

colour of the 1,2-diazepines. Furthermore, a high intensity, low wavelength band appears at λ_{max} 220 nm. These two bands are typical for the non-bonding and π electrons of the diazepine ring; they are similar in shape and intensities with those found for oxepines [11] and azepines [12]. For the *N*-benzoyldiazepines an additional band, due to the benzoyl moiety, appears at about λ_{max} 280 nm.

Photochemistry of 1-iminopyridinium ylides substituted at C(3) with electron-donating groups: non-regiospecific ring enlargement process. – Because of mesomeric or hyperconjugative effects, electron-donating substituents show no or only little orienting effects upon the photo-induced ring expansion of the corresponding ylides. Two photo-isomers are obtained in high yield *(Table 3)*, namely the 4-substituted diazepines **9d–k** and the 6-substituted diazepines **10d–k** *(Scheme 4)* which could be separated by careful column chromatography.

Scheme 4



Structural elucidation of the various pairs of isomers **9d–k** and **10d–k** is easily achieved by examination of ^{1}H-NMR. signals of the ring hydrogen atoms. The 100 MHz ^{1}H-NMR. spectra of 4-bromodiazepine **9g** and of 6-bromodiazepine **10g** *(Fig. 1)* show that structural assignments are unambiguous. ^{1}H- and ^{13}C-NMR. spectral data of the newly described diazepines **9** and **10** are given in *Tables 4* and *5*. Diazepines **9d–i** present doublets ($^1J_{C-H}$) for C(3), C(5), C(6) and C(7), whereas a singlet appears for the substituted C(4). Diazepines **10d–i** present a singlet for the substituted C(6) and doublets ($^1J_{C-H}$) for the other ring carbon atoms.

Table 4. *^{1}H-NMR. spectra of 1,2-diazepines* **9e–k** *and* **10e–k**[a])

	H–C(4)	H–C(5)	H–C(6)	H–C(7)
9e	–	6.2; *d*×*d*, *J* = 13, 7	5.7; *d*×*d*, *J* = 13, 7	6.25; *d*, *J* = 7.5
10e	6.5; *m*	6.5; *m*	–	6.5; *m*
9f	–	6.73; *d*, *J* = 6.0	5.75; *d*×*d*, *J* = 6, 7.5	6.48; *d*, *J* = 7.5
10f	6.35; *d*×*d*, *J* = 12, 4.5	6.55; *d*, *J* = 12	–	6.65; *s*
9g	–	6.9; *d*, *J* = 5.5	5.65; *d*×*d*, *J* = 5.5, 7.5	6.5; *d*, *J* = 7.5
10g	6.3; *d*×*d*, *J* = 11, 3.0	6.7; *d*, *J* = 11	–	6.7; *s*
9h	–	7.2; *d*, *J* = 6	5.7; *d*×*d*, *J* = 6.0, 8.0	6.6; *d*, *J* = 8.0
10h	6.2; *d*×*d*, *J* = 12, 4	6.85; *d*, *J* = 12	–	6.75; *s*
9i	–	6.55; *d*, *J* = 6.5	5.95; *d*×*d*, *J* = 6.5, 8.0	6.65; *d*, *J* = 8.0
10i	6.65; *m*	6.65; *m*	–	6.65; *m*
9j	–	6.95; *d*, *J* = 6	6; *d*×*d*, *J* = 6, 7.5	6.75; *d*, *J* = 7.5
10j	6.55; *m*	6.55; *m*	–	6.8; *s*
9k	–	6.9; *d*, *J* = 6	5.95; *d*×*d*, *J* = 6, 8	6.55; *d*, *J* = 8
10k	6.6; *d*×*d*, *J* = 11, 3	7.05; *d*, *J* = 11	–	6.8; *s*

[a]) Measured in $CDCl_3$ [δ ppm; *J* Hz]; spectra of compounds **9d** and **10d**, see [10].

Table 5. *^{13}C-NMR. spectral data of diazepines* **9e–i** *and* **10e–i** ($CDCl_3$)[a]

	C(3)	C(4)	C(5)	C(6)	C(7)
9e	153.24; *d*	159.0; *s*	117.64; *d*	116.23; *d*	130.6; *d*
10e	158.42; *d*	130.90; *d*	132.53; *d*	155.60; *s*	117.79; *d*
9f	157.05; *d*	133.86; *s*	136.59; *d*	118.11; *d*	133.67; *d*
10f	158.45; *d*	130.17; *d*	139.61; *d*	126.35; *s*	130.97; *d*
9g	158.32; *d*	122.94; *s*	140.43; *d*	119.16; *d*	134.11; *d*
10g	158.37; *d*	130.03; *d*	141.37; *d*	114.39; *s*	133.27; *d*
9h	161.46; *d*	96.76; *s*	148.06; *d*	120.61; *d*	135.02; *d*
10h	158.32; *d*	129.5; *d*	145.5; *d*	86.27; *s*	138.65; *d*
9i	156.60; *d*	149.53; *s*	125.92; *d*	116.88; *d*	132.23; *d*
10i	159.16; *d*	129.74; *d*	136.70; *d*	143.76; *s*	125.17; *d*

[a]) δ ppm; internal standard TMS.

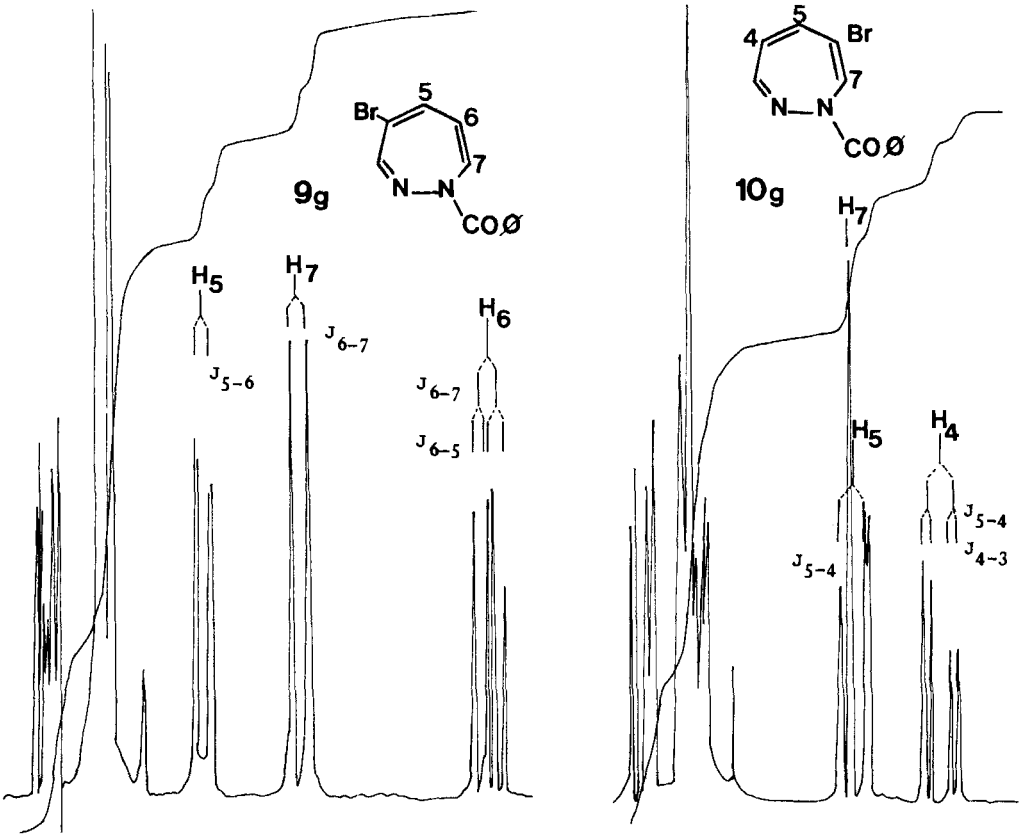
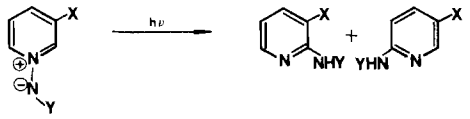


Fig. 1. *100 MHz ^1H-NMR. spectra of 4-bromodiazepine* **9g** *and 6-bromodiazepine* **10g**

Photo-isomerisation of some 3-substituted 1-iminopyridinium ylides without ring expansion: a non-regiospecific process leading to 2-aminopyridine derivatives. – The 1-iminopyridinium ylides **7l–o**, which all bear electron-donating groups at C(3), do not lead to diazepines when excited by UV. light; simple isomerization occurs, *i.e.* the N–Y group shifts to C(2) whereby 2-benzoylaminopyridines are formed. These photo-induced isomerizations are non-regiospecific processes, since both 3- and 5-substituted 2-benzoylaminopyridines are obtained *(Scheme 5)* in good to moderate yields *(Table 6)*.

Scheme 5



10l–o **11l–o** **12l–o**

Structural assignments for compounds **11l–o** and **12l–o**, based on ^{1}H-NMR. and chemical data, are unambiguous (some of the 2-aminopyridines are known compounds).

The 3-methoxy-1-benzoyliminopyridinium ylide **7p** constitutes a special case since UV. irradiation leads simultaneously to the expected 2-benzoylaminopyridines

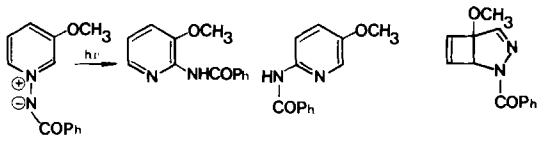
Table 6. *Spectroscopic and other data of 2-benzoylaminopyridine derivatives* **111-p, 121-p**

	Yield	M.p.	^{1}H-NMR.[b]) ($CDCl_3$)			
	[%]	[°C]	H–C(3)	H–C(4)	H–C(5)	H–C(6)
11 l	20	233–234[a])	–	7.4; *d*, *J* = 8	7.1; *d* × *d*, *J* = 8, 5	7.8; *d*, *J* = 5
12 l	30	179–180	8.2; *d*, *J* = 7	7.3; *d* × *d*, *J* = 7, 3	–	8.0; *d*, *J* = 3
11 m	25	215–216[a])	–	7.5; *m*	7.0; *d* × *d*, *J* = 7.5, 4.5	8; *d*, *J* = 4.5
12 m	17	218–219[a])	8.3; *d*, *J* = 8.5	7.2; *d* × *d*, *J* = 8.5, 3	–	7.5; *m*
11 n	23	220–221	–	7.5; *m*	7.2; *d* × *d*, *J* = 8, 4.5	7.8; *m*
12 n	33	226–227	8.2; *m*	7.3; *d* × *d*, *J* = 8, 2.5	–	8.0; *m*
11 o	36	135–136	–	7.2; *d* × *d*, *J* = 7.5, 2	6.9; *d* × *d*, *J* = 7.5, 4	7.71; *m*
12 o	24	140–141	8.0; *d*, *J* = 8.5	7.2; *d* × *d*, *J* = 8.5, 2	–	7.8; *d*, *J* = 2
11 p	19	210–211[a])	–	7.4; *m*	7.0; *d* × *d*, *J* = 7.5, 5	8.0; *m*
12 p	29	212–213[a])	8.3; *d*, *J* = 8	7.3; *d* × *d*, *J* = 8, 2	–	7.5; *m*

[a]) M.p. of the picrate. [b]) δ [ppm], *J* [Hz].

11p and **12p** *(Table 6)* and to 2-benzoyl-5-methoxy-2,3-diazabicyclo[3.2.0]hepta-3,6-diene (**13**). The latter compound is obviously a secondary photo-product arising from the corresponding 1-benzoyl-4-methoxy-1*H*-1,2-diazepine by a disrotatory electrocyclic ring closure. Similar products have already been described [10] [13].

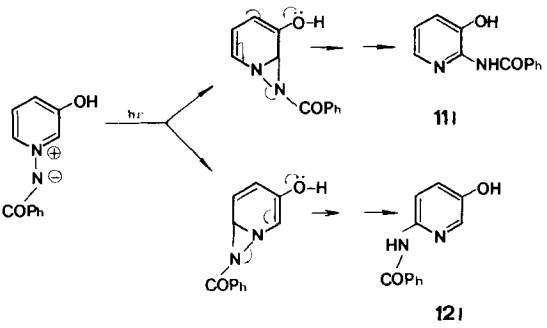
Scheme 6



The formation of 2-aminopyridines during UV. irradiation of some *N*-imino-pyridinium ylides has been described by *Snieckus et al.* [5a]. The photo-isomerization of *N*-iminoquinolinium and of *N*-imino-isoquinolinium ylides to the corresponding 2-amino-quinolines and 1-amino-isoquinolines is also known [14]. Unfortunately, no mechanism has been suggested for these photo-induced isomerizations. We favour the formation of the two possible 1,7-diazanorcaradiene intermediates. Cleavage of the N–N bond followed by a 1,2-hydrogen shift would lead to the corresponding 2-aminopyridines.

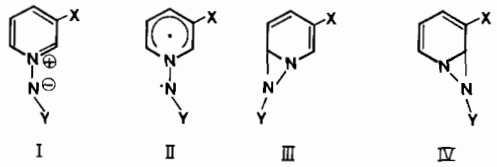
The reason why some electron-donating groups lead exclusively to diazepines and others to 2-aminopyridines only is not obvious. Nevertheless, it seems that formation of the 2-aminopyridines **11l** and **12l**, starting from ylide **7l** for example, can be interpreted as depicted in *Scheme 7*. Once more 1,7-norcaradienes seem to be the obvious intermediates. A 'push-pull' mechanism should then favour a fast and preferential cleavage of the N–N bond.

Scheme 7



Discussion. – The UV. spectrum of 1-ethoxycarbonyliminopyridinium ylide has been measured a few years ago using the stretched film technique [15]. From a *Pariser-Parr-Pople* model the two first bands – the lowest energy band being the photo-active one – could be assigned to $^*\pi_1$–π_1 transitions. Since, on the other hand, a strong negative solvatochromism is observed with 1-iminopyridinium ylides, we

Scheme 8



conclude that the lowest excitation is from the $2p_z$ orbital on the exocyclic nitrogen atom to one of the two pyridine LUMOs. This leads to a species which could be described as II, either in a singlet (*S*) or in a triplet (*T*) state. From the *T* state we may expect, either intersystem crossing to the ground state or fragmentation to a triplet nitrene [16]. In the excited *S* state, however, the two 'dot' electrons can make a new bond in the α-positions, giving either III or IV *(Scheme 8)*.

The observed regiospecific ring enlargement for electron-withdrawing substituents can be interpreted by using a HMO model. While the wave function and energy of the highest occupied molecular orbital (HOMO, π_1) is essentially unaf-

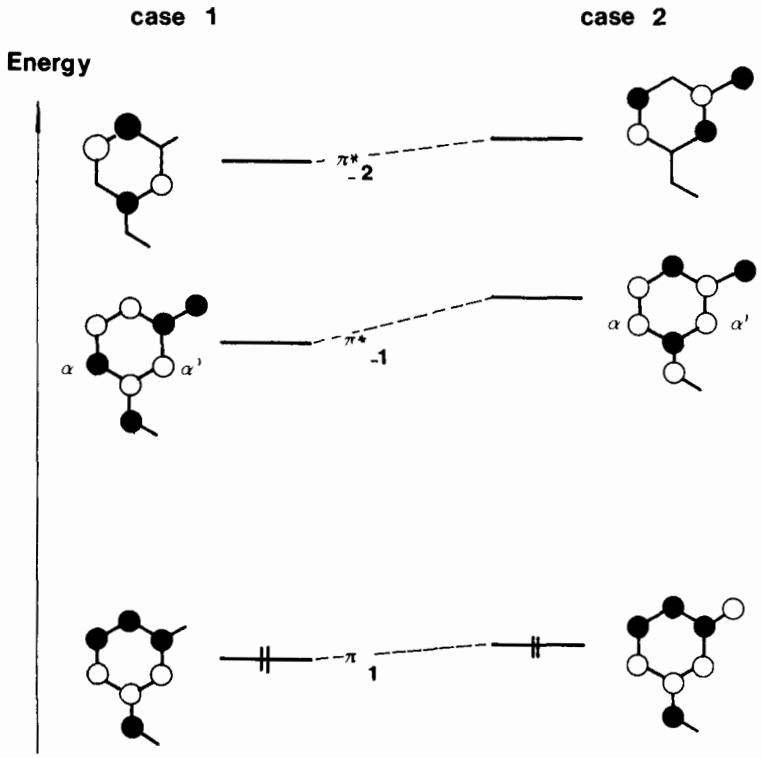


Fig. 2. *Qualitative HMO diagram for 3-substituted pyridinium ylides.* At left the perturbation (low lying π^* orbital) of the substituent dominates (case 1). At right the perturbation (high lying π orbital) is assumed to be weak (case 2).

fected by any substituent in position 3, there is a considerable effect concerning the wave function in case of the two lowest unoccupied molecular orbitals, π_{-1}^* and π_{-2}^*, as shown in *Figure 2*. Two series of substituents must be distinguished: 1) substituents with low lying π^* orbitals (X=CN, CO_2R, $CONH_2$) in position 3, and 2) substituents with (high lying) occupied orbitals (Cl, CH_2). In case 1 the substituents overrule the perturbation of the pyridinium nitrogen atom and in a first approximation the plane of symmetry of π_{-1}^* and π_{-2}^* is aligned with the C–X bond as shown in *Figure 2*. In the second case where the perturbation is weak compared to the pyridinium nitrogen atom the plane of symmetry of π_{-1}^* and π_{-2}^* is aligned with the N–N bond (*Fig. 2*, right).

Consider case 1: Exciting an electron from π_1 into π_{-1}^* (*Fig. 2*, left) will increase the bonding character between the exocyclic nitrogen atom and the carbon atom in the α-position considerable more than between the exocyclic nitrogen and the carbon atom in the α'-position (see *Fig. 2*, left). This model explains the preferential formation of 4-substituted 1*H*-1,2-diazepines in the case of electron-withdrawing substituents. In case 2 (*Fig. 2*, right) the carbon atoms in α and α'-positions are equivalent and thus no regiospecificity should be found. Therefore, halogen atoms and alkyl groups are not expected to lead to any significant regiospecificity.

We wish to thank professor *J. Michl*, University of Utah, for his suggestions and helpful discussions.

Experimental Part

Microanalyses were carried out by the *Service Central de Microanalyses* of the *C.N.R.S.* and correspond to the formulae within ±0.3%. Melting points were taken on a *Tottoli* apparatus *(Büchi)* and are corrected. UV. spectra [λ_{max} nm (ε)] were recorded on a *Beckman* DB spectrophotometer. IR. spectra (cm^{-1}) were determined on *Beckman* IR 20A and *Perkin Elmer* 1576 spectrometers. ^{1}H- and ^{13}C-NMR. spectra were obtained with *Varian* A-60-A and *Varian* XL-100/5 instruments respectively, with Me_4Si as an internal reference (δ ppm, *J* Hz). MS. were measured on a *Thomson* 208 mass spectrometer. Silica gel *(Merck)* was used for column, thin and thick layer chromatography. Abbreviations: i.V. = im Vacuum.

1. *Synthesis of 3-substituted 1-iminopyridinium ylides.* – 1.1. *N-Benzoylimino-3-cyanopyridinium ylide* (**7b**). General procedure: To a stirred solution of 1 g (0.01 mol) of 3-cyanopyridine in 30 ml of CH_2Cl_2 were added dropwise at 0° 2.1 g (0.01 mol) of mesitylsulfonylhydroxylamine in 10 ml of CH_2Cl_2. After stirring for 1 h the *N*-amino-3-cyano-pyridinium mesitylsulfonate was precipitated by addition of 30 ml of ether, filtered off and recrystallized from ethyl acetate/methanol. The salt was then dissolved in 5 ml of benzoyl chloride and heated at 80° for 24 h. The precipitate was filtered off, washed with acetone and dissolved in 2% aqueous NaOH-solution. The precipitated ylide was filtered off and recrystallized from acetone/hexane to yield 1.03 g (48%) of colourless needles. – ^{1}H-NMR. (DMSO-d_6): 7.4 [*m*, 3 H, 2 *m*- and 1 *p*-benzoyl-H]; 8.1 [*m*, 3 H, 2 *o*-benzoyl-H and 1 H–C(5)]; 8.4 [*d*, $J_{4,5}$ = 8, H–C(4)]; 8.7 [*d*, $J_{5,6}$ = 7, H–C(6)]; 8.9 [*s*, H–C(2)]. – Analysis: $C_{13}H_9N_3O$.

1.2. *N-Benzoylimino-3-carbamoylpyridinium ylide* (**7c**). A solution of 750 mg of *N*-benzoylamino-3-cyanopyridinium chloride (0.003 mol) in 5 ml of conc. HCl-solution was heated at 60° for 30 min. The reaction mixture was then cooled in an ice bath and made basic by the addition of 2% NaOH-solution. The precipitated ylide was filtered off and recrystallized from methanol to yield 500 mg (67%) of colourless needles. – ^{1}H-NMR. (DMSO-d_6): 7.4 [*m*, 3 H, 2 *m*- and 1 *p*-benzoyl-H]; 8.0 [*m*, 3 H, 2 *o*-benzoyl-H and H–C(5)]; 8.5 [*s*, 2 H, NH_2]; 8.6 [*d*, $J_{4,5}$ = 8, H–C(4)]; 9.1 [*d*, $J_{5,6}$ = 6, H–C(6)]; 9.4 [*s*, H–C(2)]. – Analysis: $C_{13}H_{11}N_3O_2$.

1.3. *N-Benzoylimino-3-fluoropyridinium ylide* (**7e**). This and the following compounds were prepared following the procedure described for ylide **7b**. – ^{1}H-NMR. (DMSO-d_6): 7.4 [*m*, 3 H, *m*- and

p-benzoyl-H]; 8.05 [*m*, 4 H, 2 *o*-benzoyl-H, H–C(4) and H–C(5)]; 8.75 [*d*, $J_{5,6}$ = 6, H–C(6)]; 9.2 [*m*, H–C(2)]. – Analysis: $C_{12}H_9FN_2O$.

1.4. N-*Benzoylimino-3-chloropyridinium ylide* (**7f**). – ^{1}H-NMR. (DMSO-d_6): 7.35 [*m*, 3 H, 2 *m*- and 1 *p*-benzoyl-H]; 7.85 [*d*×*d*, $J_{5,4}$ = 8.5, $J_{5,6}$ = 6, H–C(5)]; 8.0 [*m*, 2 H, 2 *o*-benzoyl-H]; 8.25 [*d*, $J_{4,5}$ = 8.5, H–C(4)]; 8.75 [*d*, $J_{6,5}$ = 6, H–C(6)]; 9.25 [*s*, H–C(2)]. – Analysis: $C_{12}H_9ClN_2O$.

1.5. N-*Benzoylimino-3-bromopyridinium ylide* (**7g**). – ^{1}H-NMR. (DMSO-d_6): 7.3 [*m*, 3 H, *m*- and *p*-benzoyl-H]; 7.8 [*m*, 3 H, 2 *o*-benzoyl-H and H–C(5)]; 8.3 [*d*, $J_{4,5}$ = 8, H–C(4)]; 8.7 [*d*, $J_{6,5}$ = 6, H–C(6)]; 9.2 [*s*, H–C(2)]. – Analysis: $C_{12}H_9BrN_2O$.

1.6. N-*Benzoylimino-3-iodopyridinium ylide* (**7h**). – ^{1}H-NMR. (DMSO-d_6): 7.4 [*m*, 3 H, 2*m*- and 1 *p*-benzoyl-H]; 7.65 [*d*×*d*, $J_{5,6}$ = 6, $J_{5,4}$ = 8, H–C(5)]; 8.0 [*m*, 2 H, 2 *o*-benzoyl-H]; 8.5 [*d*, $J_{4,5}$ = 8, H–C(4)]; 8.8 [*d*, $J_{6,5}$ = 6, H–C(6)]; 9.25 [*s*, H–C(2)]. – Analysis: $C_{12}H_9IN_2O$.

1.7. N-*Benzoylimino-3-benzoyloxypyridinium ylide* (**7i**). – ^{1}H-NMR. (DMSO-d_6): 7.7 [*m*, 12 H, 10 benzoyl-H, H–C(4) and H–C(5)]; 8.9 [*d*, $J_{6,5}$ = 6, H–C(6)]; 9.2 [*s*, H–C(2)]. – Analysis: $C_{19}H_{14}N_2O_3$.

1.8. N-*Benzoylimino-3-succinimidopyridinium ylide* (**7j**). – ^{1}H-NMR. (DMSO-d_6): 2.8 [*s*, 4 H, 2 CH_2]; 7.4 [*m*, 3 H, 2 *m*- and 1 *p*-benzoyl-H]; 8.1 [*m*, 4 H, 2 *o*-benzoyl, H–C(4) and H–C(5)]; 9.0 [*m*, H–C(2) and H–C(6)]. – Analysis: $C_{16}H_{13}N_3O_3$.

1.9. N-*Benzoylimino-3-phenylpyridinium ylide* (**7k**). – ^{1}H-NMR. (DMSO-d_6): 7.8 [*m*; 12 H, 10 Phenyl-H, H–C(4) and H–C(5)]; 8.8 [*d*, $J_{6,5}$ = 6, H–C(6)]; 9.05 [*s*, H–C(2)]. – MS.: 274 (M^+).

1.10. N-*Benzoylimino-3-hydroxypyridinium ylide* (**7l**). – ^{1}H-NMR. (DMSO-d_6): 7.4 [*m*, 3 H, 2 *m*- and 1 *p*-benzoyl-H]; 7.6 [*m*, H–C(4) and H–C(5)]; 8.0 [*m*, 2 H, 2 *o*-benzoyl-H]; 8.3 [*m*, H–C(2) and H–C(6)]. – Analysis: $C_{12}H_{10}N_2O_2$.

1.11. N-*Benzoylimino-3-dimethylaminopyridinium ylide* (**7m**). – ^{1}H-NMR. (DMSO-d_6): 3.0 [*s*, 6 H, 2 N–CH_3]; 7.1 [*d*×*d*, $J_{4,5}$ = 9, $J_{4,6}$ = 3, H–C(4)]; 7.4 [*m*, 4 H, 2 *m*-, 1 *p*-benzoyl-H and H–C(5)]; 8.2 [*m*, 4 H, 2 *o*-benzoyl-H, H–C(2) and H–C(6)]. – Analysis: $C_{14}H_{15}N_3O$.

1.12. N-*Benzoylimino-3-benzoylaminopyridinium ylide* (**7n**). – ^{1}H-NMR. (DMSO-d_6): 7.6 [*m*, 6 H, 2×2 *m*- and 2×1 *p*-benzoyl-H]; 8.1 [*m*, 5 H, 2×2 *o*-benzoyl-H and H–C(5)]; 8.5 [*d*, $J_{4,5}$ = 9, 1H, H–C(4)]; 8.55 [*d*, $J_{6,5}$ = 6, H–C(6)]; 9.4 [*s*, H–C(2)]; 11.1 [*s*, NH]. – Analysis: $C_{19}N_{15}N_3O_2$.

1.13. N-*Benzoylimino-3-aminopyridinium ylide* (**7o**). A solution of 730 mg of *N*-benzoylimino-3-benzoylaminopyridinium ylide (**7n**) (0.0023 mol) in 10 ml of 5% aqueous KOH-solution was heated at 90° for 4 h, then filtered and evaporated i.V. Recrystallization of the residue from a mixture of acetone/hexane 7:3 yielded 464 mg (95%) of colourless needles. – ^{1}H-NMR. (DMSO-d_6): 6.2 [*s*, NH_2]; 7.4 [*m*, 5 H, 2 *m*- and 1 *p*-benzoyl-H, H–C(4) and H–C(5)]; 8.0 [*m*, 4 H, 2 *o*-benzoyl-H, H–C(2) and H–C(6)]. – MS.: 213 (M^+).

1.14. N-*Benzoylimino-3-methoxypyridinium ylide* (**7p**). A solution of 3.6 g of *N*-benzoylimino-3-hydroxypyridinium ylide (**7l**) (0.017 mol) in 15 ml of *t*-butyl alcohol was added dropwise to 1 g (0.024 mol) of diazomethane in 5 ml of ether at – 10°. The reaction mixture was stirred overnight at RT., concentrated i.V. to 5 ml then treated with a mixture of 3.5 ml of 6N ethanolic HCl and 15 ml of petroleum ether. The precipitated *N*-benzoylimino-3-methoxypyridinium hydrochloride was filtered off, dissolved in 20 ml of water and the resulting solution was made alkaline by addition of 2% NaOH-solution. Extraction with $CHCl_3$, evaporation of the organic phase i.V. and recrystallization from acetone/hexane 7:3 yielded 1.14 g (28%) of colourless needles. – ^{1}H-NMR. (DMSO-d_6): 7.45 [*m*, 3 H, 2 *m*- and 1 *p*-benzoyl-H]; 7.8 [*m*, H–C(4) and H–C(5)]; 8.0 [*m*, 2 H, 2 *o*-benzoyl-H]; 8.5 [*m*, H–C(2) and H–C(6)]. – Analysis: $C_{13}H_{12}N_2O_2$.

2. *Synthesis of 1H-1,2-diazepines.* – 2.1. N-*Benzoyl-4-cyano-1H-1,2-diazepine* (**8b**). General procedure: The solution of 1 g (0.004 mol) of ylide **7b** in 500 ml of benzene was irradiated in a Pyrex immersion-well photoreactor with a *Philips* HPK 125 lamp. After 15 h of irradiation the solvent was evaporated i.V. and the residue recrystallized from cyclohexane to afford 840 mg (84%) of orange prisms. – IR. (KBr): 1645 (C=O). – MS.: 223 (M^+).

2.2. N-*Benzoyl-4-carbamoyl-1H-1,2-diazepine* (**8c**). This and the following compounds were prepared following the general procedure described in 2.1. – IR. (KBr): 1690 and 1665. – MS.: 241 (M^+).

2.3. N-*Benzoyl-4-fluoro-1*H-*1,2-diazepine* (**9e**) *and* N-*benzoyl-6-fluoro-1*H-*1,2-diazepine* (**10e**). These compounds were separated by column chromatography using cyclohexane/ethyl acetate 7:3. – IR. (KBr): **9e**: 1655 (C=O); **10e**: 1660 (C=O). – Analysis: $C_{12}H_9FN_2O$.

2.4. N-*benzoyl-4-chloro-1*H-*1,2-diazepine* (**9f**) *and* N-*benzoyl-6-chloro-1*H-*1,2-diazepine* (**10f**). – IR. (KBr): **9f**: 1660 (C=O); **10f**: 1660 (C=O). – Analysis: $C_{12}H_9ClN_2O$.

2.5. N-*Benzoyl-4-bromo-1*H-*1,2-diazepine* (**9g**) *and* N-*benzoyl-6-bromo-1*H-*1,2-diazepine* (**10g**). – IR. (KBr): **9g**: 1655 (C=O); **10g**: 1650 (C=O). – Analysis: $C_{12}H_9BrN_2O$.

2.6. N-*Benzoyl-4-iodo-1*H-*1,2-diazepine* (**9h**) *and* N-*benzoyl-6-iodo-1*H-*1,2-diazepine* (**10h**). – IR. (KBr): **9h**: 1655 (C=O); **10h**: 1655 (C=O). – Analysis: $C_{12}H_9IN_2O$.

2.7. N-*Benzoyl-6-benzoyloxy-1*H-*1,2-diazepine* (**9i**) *and* N-*benzoyl-6-benzoyloxy-1*H-*1,2-diazepine* (**10i**). – IR. (KBr): **9i**: 1730 and 1660 (C=O); **10i**: 1740 and 1675 (C=O). – Analysis: $C_{19}H_{14}N_2O_3$.

2.8. N-*Benzoyl-4-succinimido-1*H-*1,2-diazepine* (**9j**) *and* N-*benzoyl-6-succinimido-1*H-*1,2-diazepine* (**10j**). – IR. (KBr): **9j**: 1705 and 1665 (C=O); **10j**: 1710 and 1633 (C=O). – Analysis: $C_{16}H_{13}N_3O_3$.

2.9. N-*Benzoyl-4-phenyl-1*H-*1,2-diazepine* (**9k**) *and* N-*benzoyl-6-phenyl-1*H-*1,2-diazepine* (**10k**). – IR. (KBr): **9k**: 1665 (C=O); **10k**: 1655 (C=O).

3. *Synthesis of 2-benzoylaminopyridines.* – Irradiation of ylides 7l–**o** using the same general conditions as described for compound **7b** (2.1) afforded the 2-benzoylaminopyridine derivatives **11l–o** and **12l–o** (for yields, physical and spectroscopic data see *Table 6*).

4. *Irradiation of* N-*benzoylimino-3-methoxypyridinium ylide* (7**p**). Irradiation of ylide 7**p** under the general experimental conditions described afforded the 2-benzoylaminopyridines **11p** and **12p** (see *Table 6*) and a colourless oil identified as 2-benzoyl-5-methoxy-2,3-diazabicyclo[3.2.0]hepta-3,6-diene (**13**). Yield: 20%. – UV. (EtOH): 301 (1900), 265 (10300), 230 (9400). – IR. (KBr): 1640 (C=O). – ^{1}H-NMR. ($CDCl_3$): 3.45 [*s*, OCH_3]; 5.4 [*d*, $J_{1,6}$ = 1, H–C(1)]; 6.2 [*d*, $J_{6,7}$ = 3, H–C(7)]; 6.65 [*d*×*d*, $J_{6,1}$ = 1, $J_{6,7}$ = 3, H–C(6)]; 7.5 [*m*, H–C(4)]; 7.5 [*m*, 3 H, 2 *m*- and 1 *p*-benzoyl-H]; 7.95 [*m*, 2 H, 2 *o*-benzoyl-H]. – MS.: 228 (M^+).

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