

THE PHOTOCHEMISTRY OF AROMATIC-N-YLIDES.
REARRANGEMENT AND FRAGMENTATION PATTERNS.

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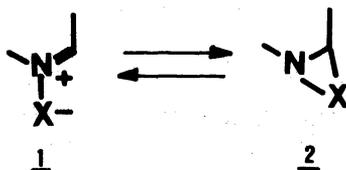
Abstract - Rearrangement and fragmentation patterns, which have been observed during uv. irradiation of the following pyridinium ylides, will be discussed: pyridinium methylides, N-iminopyridinium ylides and pyridine-N-oxides. As a rule these mesoionic compounds undergo two competing reactions: i) photolytic cleavage via a triplet state, leading to the corresponding pyridines and to carbenes, nitrenes and oxene respectively; ii) photochemical rearrangement via an excited singlet state, leading either to ring contraction, to ring enlargement or to ring cleavage.

The photochemistry of N-iminopyridinium ylides has been studied in detail, since the photoinduced rearrangement pattern leads in high yield to the isomeric 1,2-diazepines. Overall quantum yield of this ring enlargement process is low. In order to interpret the uv spectra of these 1-iminopyridinium ylides, their dichroism has been measured using Egger's stretched film technique. Solvent effects and a Pariser-Parr-Pople model point to $\pi-\pi^*$ transitions for the photoactive band, possibly followed by intramolecular charge transfer.

1,2-Diazepines are thought to occur photochemically via 1,7-diazanorcaradienes and proved to be excellent synthons for the buildup of new polycyclic molecules.

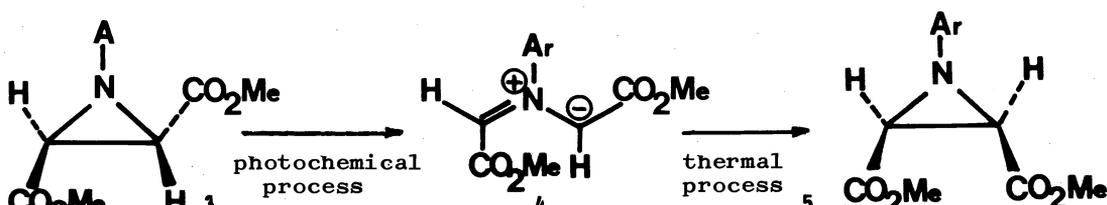
INTRODUCTION

Electrocyclic ring closure of 4 π electron 1,3-dipolar species 1, leading to the corresponding three-membered ring isomers 2, is permitted, both by thermal and by photochemical processes according to symmetry selection rules (Ref. 1). These latter ones should be preferred, since three-membered rings are usually unstable when heated, although some exceptions are known (Ref. 2). In view of their aromatic counterparts we shall be dealing with (*vide infra*), three types of 1,3-dipoles 1 are of interest to us: azomethine ylides ($X = CR_2$); azomethine imines ($X = NR$) and nitrones ($X = O$). Electrocyclic ring closure would lead to the correspon-

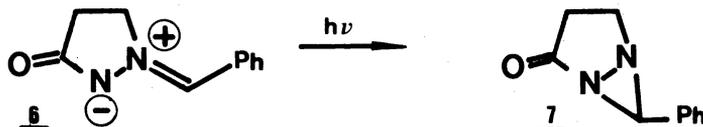


ding three-membered rings 2: aziridines ($X = CR_2$), diaziridines ($X = NR$) and oxaziridines ($X = O$).

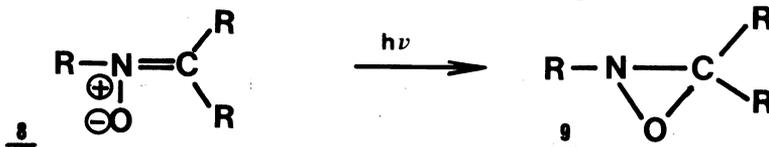
Substituted aziridines 3 and 5 are known to be much more stable than the corresponding azomethine ylides, as was shown by Huisgen (Ref. 2) who trapped the latter by cycloaddition reactions with dipolarophiles and proved the concertedness of all the pericyclic reactions which are involved.



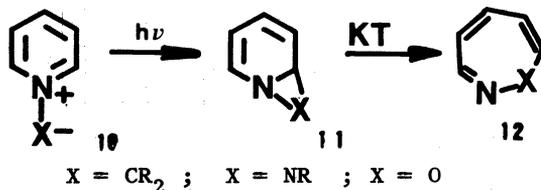
Stable azomethine imines lead photochemically to the corresponding diaziridines as was shown by Schultz (3) and by Moore (4). For example azomethine imine 6 leads to the bicyclic diaziridine 7 (Ref. 3).



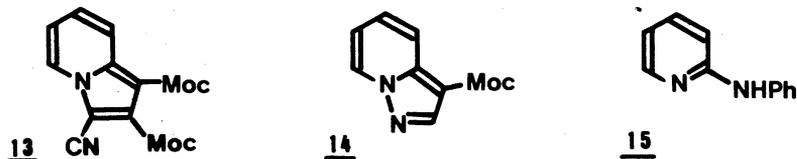
Calvin showed that photoexcitation of nitrones 8 leads, via electrocyclic ring closure, to the corresponding oxaziridines 9 (Ref. 5).



Merely as a working hypothesis we postulated several years ago that pyridinium ylides 10, namely pyridinium methylides ($X = CR_2$), N-iminopyridinium ylides ($X = NR$) and pyridine-N-oxides ($X = O$), should undergo photoinduced electrocyclic ring closure to the corresponding norcaradienes 11, in the same way the non-aromatic 1,3-dipolar species 1 underwent ring closure to their isomers 2 (Ref. 6). Rapid thermal and disrotatory valence tautomerism of compounds 11 was expected to lead to the corresponding cycloheptatriene analogues 12. Predicting a similar behaviour for pyridinium ylides 10 and for 1,3-dipoles 1 in their excited state seemed reasonable in view of the fact that both types of compounds lead to 1,3-dipolar cycloaddition reactions (Ref. 7); in the aromatic series pyridinium dicyanomethylide reacts with methyl acetylene dicarboxylate leading to the aromatic adduct 13 after HCN elimination (Ref. 8). Likewise the non-substituted and rather unstable 1-iminopyridinium ylide reacts with methyl propynoate and gives adduct 14 (Ref. 8). Pyridine-N-oxide reacts with phenylisocyanate and leads to 2-phenylaminopyridine 15 via an oxadiazolidinone intermediate which expells CO₂ (Ref. 8).



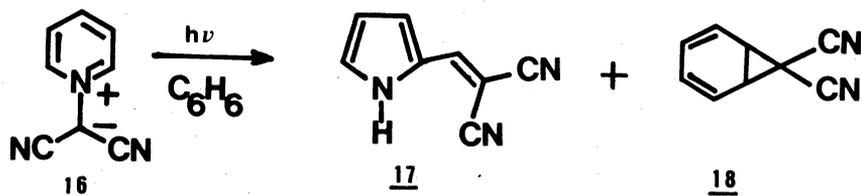
As will be seen below uv excitation of 1-iminopyridinium ylides leads to the expected 1,2-diazepines 12 ($X = NR$). Pyridinium methylides and pyridine-N-oxides give pyrrole derivatives, the formation of which is best explained by assuming the intermediate occurrence of 2H-azepines 12 ($X = CR_2$) and 1,2-oxazepines 12 ($X = O$) respectively.



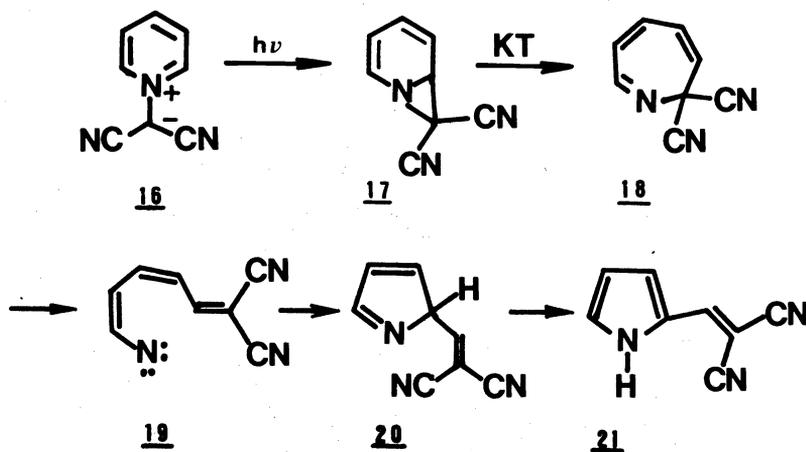
THE PHOTOCHEMISTRY OF PYRIDINIUM METHYLIDES

The photochemistry of several pyridinium methylides has been investigated, albeit without much success. An interesting spectroscopic phenomenon is observed which occurs also with other pyridinium ylides: the longest lying absorption band, which happens to be the photoactive part of the absorption spectrum, undergoes a hypsochromic shift when solvent polarity is increased. This negative solvatochromism, which would be a prima facie evidence in favour of an $n-\pi^*$ transition for ketones, must be accounted for in a different way since the extinction coefficients are far too high (by several thousands). Negative solvatochromism with high extinction coefficients is believed to rather account for $\pi-\pi^*$ transitions leading to intramolecular charge transfer as will be seen later with 1-iminopyridinium ylides.

Ultra-violet irradiation of pyridinium dicyanomethylide 16 in benzene, using mercury high pressure lamps and PYREX filters, leads to pyrrole isomer 17 and to 7,7-dicyanonorcaradiene 18 (Ref. 9). Compound 18 obviously occurs from a photoinduced dicyanocarbene transfer reaction to benzene, whereas photoisomer 17 stems from a complex photorearrangement process.

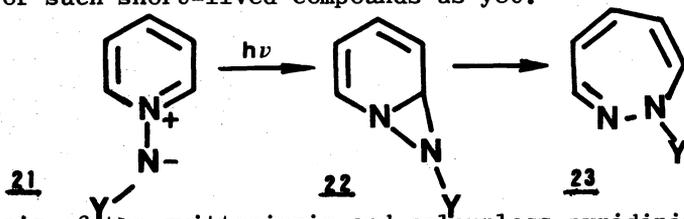


Irradiation of 16 in chloroform solution in the presence of cis or trans 4-methyl-2-pentene leads, albeit in poor yield, to a mixture of cis and trans 1,1-dicyano-2-isopropyl-3-methylcyclopropane, a result which points to the intermediate occurrence of dicyanocarbene, either in a triplet state or as a mixture of singlet and triplet states (Ref. 10). The formation of pyrrole 17 is best explained by assuming the occurrence of the vinylic nitrene intermediate 19 which could result from ring opening of norcaradiene 17 or of azepine 18. Intramolecular cyclisation of 19 would then lead to pyrrolene 20 and thence to pyrrole 17.



THE PHOTOCHEMISTRY OF 1-IMINOPYRIDINIUM YLIDES

1-Iminopyridinium ylides **2** proved to be the most interesting pyridinium ylides **10** in terms of preparative organic photochemistry. Furthermore the major photoproduct had the predicted seven-membered 1,2-diazepine structure **23** (Ref. 11). According to our hypothetical mechanistic scheme 1,7-diazanorcaradienes **22** are supposed to be intermediates on the reaction pathway leading from **21** to **23** (Ref. 6 and 12), although there is no clearcut proof in favour of such short-lived compounds as yet.



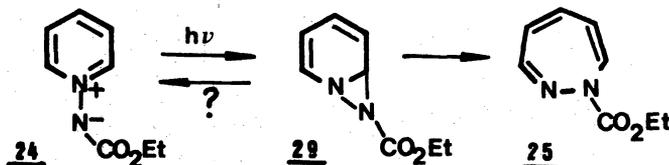
The synthesis of the zwitterionic and colourless pyridinium ylides **21** is based on nitrogen-nitrogen coupling reactions. They involve nitrene derivatives, which are obtained from azido compounds like ethyl azidoformate (**13**), or O-sulfonylated hydroxylamines, like hydroxylamine-O-sulfonic acid (Ref.14) or, even better, mesitylsulfonylhydroxylamine (Ref. 15).

Various chromophores have been attached to the pyridine nitrogen atom: alkoxycarbonylimino-, benzoylimino- and tosylimino- groups. Ylides **21** all lead in high chemical yield to the corresponding 1,2-diazepines (Table 1) when irradiated by means of high pressure mercury vapour lamps through Pyrex glass. As can be seen from Table 1 1-iminopyridinium ylides have a strong absorption band which appears at about 320 nm. in methanol solution. Again a strong negative solvatochromism is observed which is typical of all pyridinium ylides **10**. Let us mention that the empirical solvent polarity scale, as defined by Kosower (Z parameters) and by Dimroth (E_T parameters) has been set up by using a zwitterionic species which is an arylogue of a substituted pyridine-N-oxide (Ref. 16).

TABLE 1. Absorption spectra, blueshift and photochemical ring enlargement of some 1-iminopyridinium ylides.

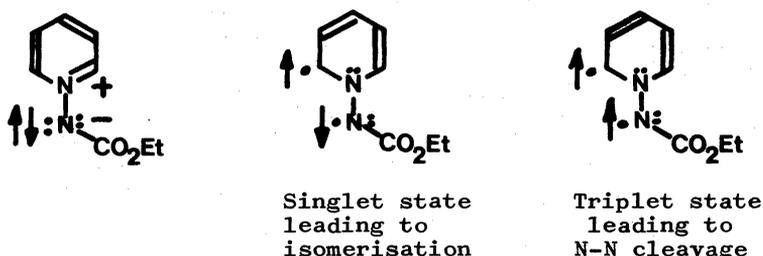
| λ_{max} nm (ϵ) | |
|---|--|
| 316 (5,000) in MeOH | |
| 344 (5,300) in C ₆ H ₆ | |
| 319 (5,000) in MeOH | |
| 322 (3,800) in MeOH | |

Overall quantum yields proved to be low: 3.5% measured in methanol for the disappearance of ylide **24** (Ref. 10). In our opinion this could be an indication in favour of the reversible formation of diazanorcaradiene **29** which may either revert to the ylide **24** or ring tautomerize to the diazepine **25**, the first process being the fastest one.



In order to interpret the electronic spectrum of ylides 10 we have measured the dichroism of 1-ethoxycarbonyliminopyridinium ylide 24, oriented in a stretched polyvinylalcohol film according to Egger's method (Ref. 17). If the carbonyl group is assumed to be coplanar with the aromatic ring, only two important conformations have to be taken into consideration. In view of the high observed dichroism, it seems reasonable to assume that the " elongated " conformation prevails with the long axis of the molecule nearly parallel to the N-N bond. Unambiguous assignment of the polarization direction from the experimental curves, which have been obtained with Egger's method, requires at least C_{2v} molecular symmetry. Since 24 has at most C_s symmetry the observed results are only approximate in character. Since it proved possible to reduce the perpendicular component of the first band (photoactive band) but not the parallel component, we infer that the vector of the first transition is approximately parallel to the long axis of the molecule in the elongated conformation. This result points to a $\pi-\pi^*$ transition (Ref. 18).

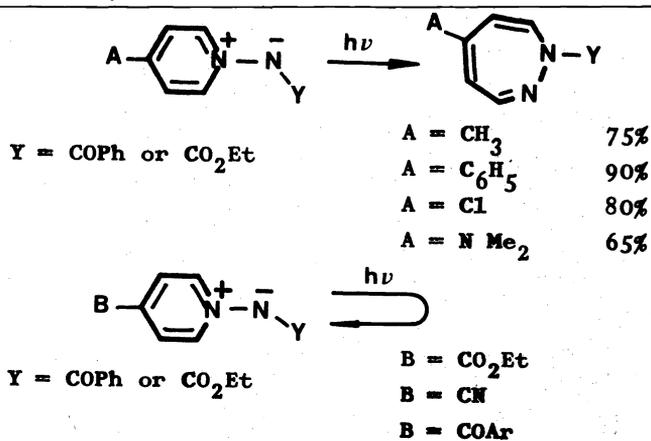
LCAO-SCF-CI calculations of the Pariser-Parr-Pople type predict $\pi-\pi^*$ transitions for the photoactive part of the absorption spectrum: energies, relative intensities and polarization directions agree quite well with the experimental results, assuming an excited singlet state to be responsible for the photoisomerisation process (Ref. 18). Experiments carried out so far suggest that this is indeed the case (*vide infra*). The results obtained from theoretical calculations are that on excitation negative charge is being transferred from the exocyclic ylide nitrogen to the ring. In view of the strong negative solvatochromism, one may assume that intramolecular charge transfer occurs, leading to some sort of a diradical species. In its singlet this diradical could ring close to the diazanorcaradiene 29; intersystem crossing would lead to a triplet and thence to homolytic N-N bond cleavage.



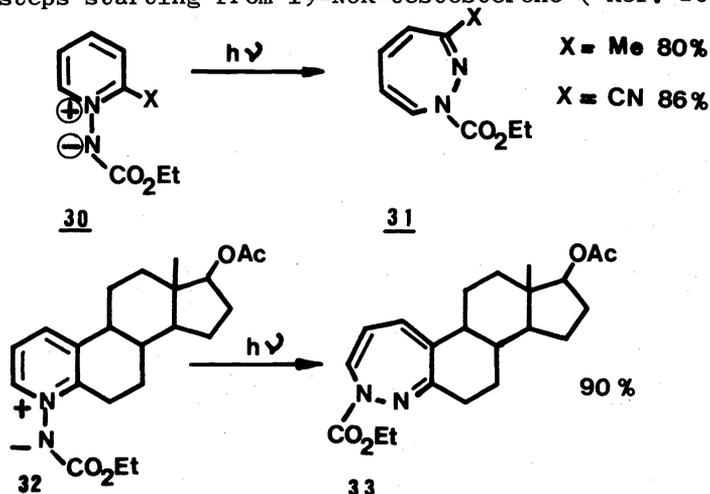
The photochemical synthesis of 1,2-diazepines as described above is of preparative interest to organic chemists (Ref. 19). Large batches of diazepines are prepared by using a 2000 watt photoreactor which has been developed by CIBA-GEIGY in Basel.

Ring monosubstituted pyridinium ylides are of interest to test substituent effects upon their photochemical reactivity. From data collected on Table 2 we deduce that the mesomeric effect of substituents attached to C-4 of the pyridinium ylide ring is pronounced indeed: electron-donating groups like dimethylamin, chlorine and phenyl permit photoinduced ring expansion, whereas electron-attracting groups like ketones, esters or nitriles inhibit this process (Ref. 19).

TABLE 2. Photochemical behaviour of 4-substituted 1-iminopyridinium ylides.

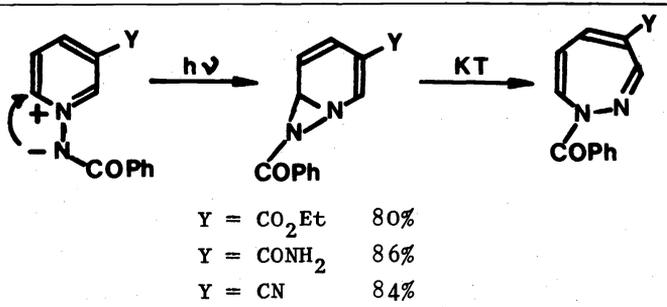


Substituents attached to C-2 or to C-3 of the pyridinium ring could lead to two isomeric diazepines depending upon the cyclisation direction of the exocyclic nitrogen atom: toward C-2 or toward C-6. 2-Chloro- or 2-methoxy-pyridinium ylides could not be synthesized. 2-Cyanopyridinium ylide **30** (X = CN) undergoes in high yield a regiospecific ring enlargement leading exclusively to 3-cyano-1-ethoxycarbonyl-1,2-diazepine **31** (X = CN) (19). Rather unexpectedly the 2-methylpyridinium ylide **30** (X = CH₃) leads to the same type of result: again one observes a regiospecific ring³enlargement to 1,2-diazepine **31** (X = CH₃). Methyl groups having no pronounced electronic effect upon π electrons, it is assumed that the regiospecific ring enlargement is mainly due to a steric effect which would prevent ring closure of the exocyclic nitrogen atom to occur toward C-2 (Ref. 19). Along these same lines the steroidal 1,2-diazepine **33** could be synthesized regiospecifically and in high yield from ylide **32**, this latter compound having been obtained in several steps starting from 19-NOR-testosterone (Ref. 20).



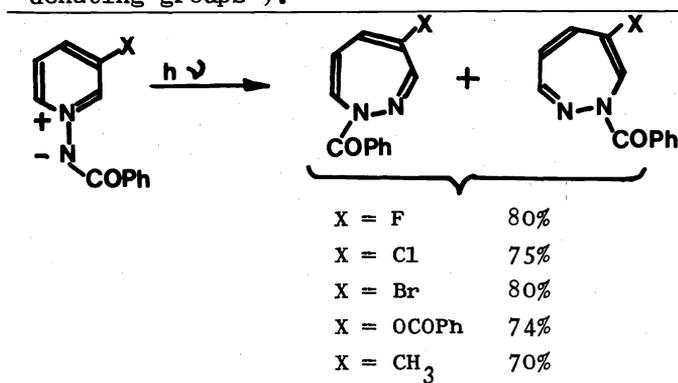
3-Substituted pyridinium ylides are obviously devoid of any such steric interference during the diazanorcaradiene formation step. Therefore it was assumed that π electronic effects would not be hampered by steric interference. As can be seen from Table 3 electron-attracting groups like esters, amides and nitriles lead regiospecifically and in high yield to only one type of photoisomer, namely 4-substituted 1,4-diazepines. Up to now no satisfactory explanation can be put forward in order to account for this regiospecific ring expansion (Ref. 21).

TABLE 3. Regiospecific photochemical ring expansion of 3-substituted pyridinium ylides (Y = π electron-attracting groups).



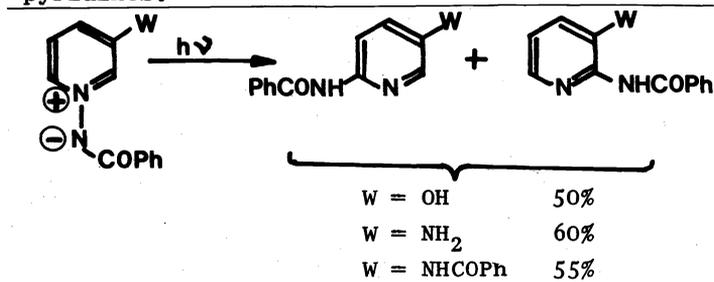
To the contrary, electron-donating C-3 substituents, which do not bear any acidic hydrogen atoms, lead in a non-regiospecific way and in high yield to a mixture of the corresponding 4- and 6-substituted 1,2-diazepines (Table 4) (Ref. 21).

TABLE 4. Non-regiospecific photochemical ring expansion of 3-substituted pyridinium ylides (Y = electron-donating groups).

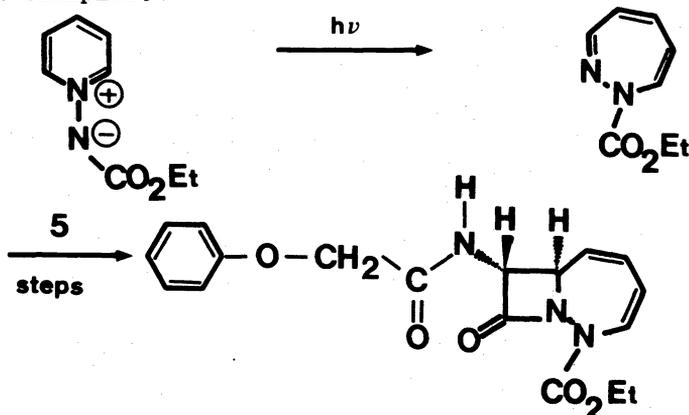


The photochemistry of 3-substituted pyridinium ylides, which bear acidic hydrogen atoms at the site of the electron-donating groups, do not lead to any diazepines. Instead one obtains a mixture of two isomeric 2-aminopyridines as can be seen from Table 5. The formation of these two types of isomers can be explained in terms of a non-regiospecific electrocyclicisation of the exocyclic nitrogen atom toward C-2 and toward C-6, followed by a prototropy and the opening of the norcaradiene diaziridine rings. Alternatively one may also assume a non-regiospecific photoinduced 1,2-sigmatropic shift of the benzoylimino group to C-2 and C-6, followed by a prototropy.

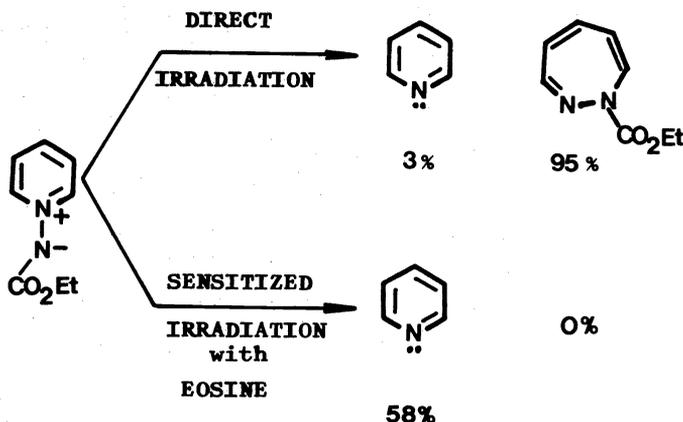
TABLE 5. Non-regiospecific photochemical isomerisation of 3-substituted pyridinium ylides leading to 2-aminopyridines.



1,2-Diazepines being easily available by the aforementioned photoinduced ring expansion process, proved to be interesting synthons for the preparation of various polycyclic systems: acid catalysed dimerisation leads to tricyclic compounds (22); 1,3-dipoles add either to the Δ^4 or to the Δ^2 double bond leading for example to pyrazolino-diazepines and thence to homodiazepines (Ref. 23) or to oxadiazolines (Ref. 24); potential antibiotics have been synthesized in excellent yields starting from 1,2-diazepines, acyl chlorides and triethylamine (Ref. 24 and 25), to quote but a few examples.



Although photoinduced ring expansion of 1-iminopyridinium ylides toward 1,2-diazepines is by far the major reaction pathway, a photolytic N-N bond cleavage competes with this process and leads to the parent pyridines and to nitrenes. For example uv irradiation in benzene of 1-ethoxycarbonyliminopyridinium ylide 24 gives 1-ethoxycarbonyl-1,2-diazepine 25 (95 %), pyridine (3%) and 1-ethoxycarbonylazepine (2%) (Ref. 11); this latter compound initiates from ethoxycarbonylnitrene addition to benzene (Ref. 26). In the presence of a triplet sensitiser energy transfer occurs and leads only to N-N bond cleavage, no diazepine being formed at all. Therefore it is assumed that photolytic bond cleavage initiates from an excited triplet state whereas ring expansion proceeds from an excited singlet state. From phosphorescence measurements obtained with ylide 24 the energy level (61 Kcal/mole) and lifetime ($\tau = 0.25$ sec.) of the triplet state have been determined



Direct irradiation of ylide 24 performed in the presence of cis or trans 4-methyl-2-pentene in various concentrations leads to a mixture of cis and trans 1-ethoxycarbonyl-2-methyl-3-isopropylaziridine. The ratio of cis vs. trans aziridines proved to be constant irrespective of olefin concentration, proving that all nitrene formed is in its triplet state (Table 6) (Ref. 10)

TABLE 6. Cis and trans 1-ethoxycarbonyl-2-methyl-3-isopropyl aziridine formation during direct uv irradiation of ylide 24 in the presence of trans 4-methyl-2-pentene.

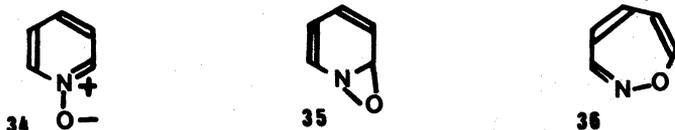
| OLEFIN conc. in mol/liter | 4.4 | 2.6 | 1.8 | 0.9 | 0.2 |
|--|-------|-------|-------|-------|-------|
| <u>[cis AZIRIDINE]</u> <u>[cis] + [trans]</u> | 19.4% | 21% | 19% | 19% | 19.1% |
| PYRIDINE YIELD | 1.44% | 1.88% | 1.70% | 1.82% | 1.56% |
| AZIRIDINE YIELD | 0.75% | 0.69% | 0.59% | 0.52% | 0.48% |

The photochemical behaviour of 1-iminopyridinium ylides proved to be most interesting in view of the fact that by direct irradiation the main reaction pathway leads to ring expansion, whereas by sensitized irradiation only N-N bond cleavage occurs.

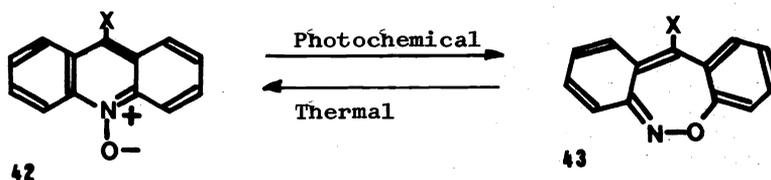
THE PHOTOCHEMISTRY OF AROMATIC N-OXIDES

The photochemistry of aromatic-N-oxides, and in particular of pyridine-N-oxides, has been investigated extensively (Ref. 27 and 28). We shall focus on a few aspects only which are closely related to the photochemistry of pyridinium methyldes and of 1-iminopyridinium ylides.

According to our initial mechanistic hypothesis, uv irradiation of pyridine-N-oxides 34 should lead to 1-aza-7-oxa-norcaradiens 35 and thence to 1,2-oxazepines 36. In two instances these seven-membered rings could be obtained: photochemistry of 9-chloro and of 9-cyanoacridine-N-oxides 42 leads to the corresponding dibenzo-1,2-oxazepines 43, which by thermal activation revert back to the starting material (Ref. 29). It would seem that these two photochemical and thermal reactions closely parallel the behaviour of 1-iminopyridinium ylides and of their isomeric 1,2-diazepines respectively, since thermal activation of 1,2-diazepines leads to the parent

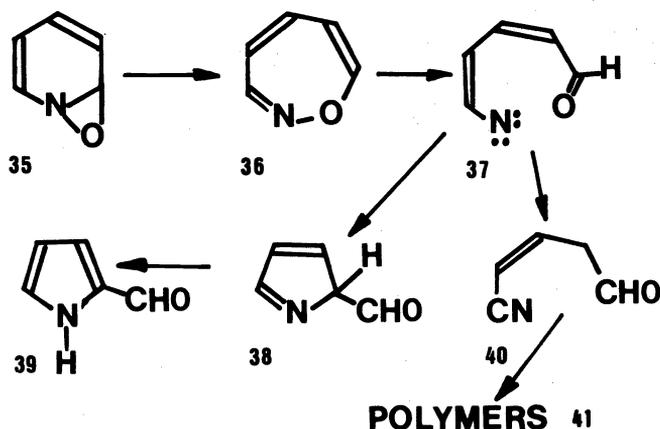


ylides (Ref. 19). These results are in good agreement with the existence of three-membered intermediates : oxaziridines and diaziridines, although to our knowledge such three-membered rings have never been detected during the photochemistry of pyridinium ylides.



Buchardt questioned the formation of such intermediates . Using nanosecond flashphotolysis with 3,6-diphenylpyridazine-N-oxide he found that the primary photoproduct is the corresponding open-chain diazoketone. In other words the oxaziridine does not form at all, the geometry of the excited hypersurface being such that no minimum corresponding to the stable three-membered ring appears. This latter structure is bypassed (Ref. 30). It remains to be seen how general these rather puzzling results are (Ref. 28).

The many photoisomers which have been isolated during the photochemistry of aromatic-N-oxides are best explained by postulating oxaziridines as primary photoproducts (Ref. 28). Again two competing reaction pathways are observed: i) photoinduced isomerisation patterns which initiate from a singlet state; ii) photolytic N-O bond cleavage which proceeds from a triplet state (Ref. 28). For example uv irradiation of pyridine-N-oxide leads to 2-formylpyrrole, to pyridine, to an insoluble polymer and to atomic oxygen transfer to solvent molecules (Ref. 31). Formation of the pyrrole isomer 39 is best explained by assuming successive occurrence of four intermediates: 1-aza-7-oxanorcaradiene 35, 1,2-oxazepine 36, vinylic nitrene 37 and pyrrolenine 38. The main product being an insoluble material which bears nitrile groups, we postulate isomerisation of the vinylic nitrene 37 to the acrylonitrile derivative 40 which would polymerise to 41. Since the photolytic reaction is enhanced by triplet sensitisers (Ref. 31 and 32), it was thought that the use of triplet quenchers would orient the photoreaction preferentially toward the ring contraction pathway. Piperylene proved to be inefficient a quencher. Therefore we turned our attention to transition metal salt complexes in which the metal is known to act as triplet quencher (Ref. 33). Copper salts proved to be the only transition metal salts to have any effect upon the photochemistry of pyridine-N-oxides: they permitted to raise dramatically the yield of 2-formylpyrrole formation (Ref. 34). Rather unexpectedly copper salts raised also the yield of the photolytic N-O bond cleavage. Therefore there is no triplet quenching involved at all. We believe that the copper cation stabilises the

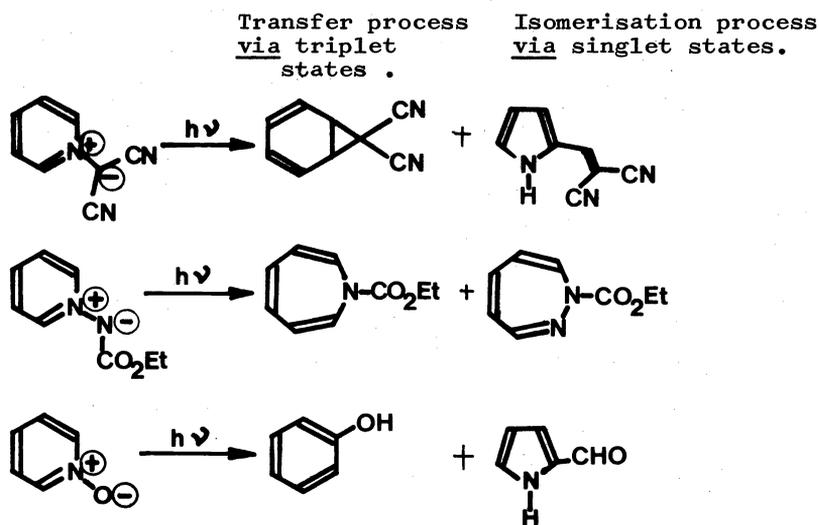


intermediate nitrene 37 and prevents it from isomerising to acrylonitrile 40. Instead ring closure to pyrroline 38 should be favoured by the same token. This intriguing copper salt effect, observed with pyridine-N-oxides in water solution, gives easy access to specifically substituted 2-formylpyrroles in preparative amounts (Ref. 34).

CONCLUSION

Real existence of the above postulated intermediates could not be proven during the uv irradiation of the three types of pyridinium ylides 10 as yet. Nevertheless in all three classes of ylides we observe two competing reaction pathways which, in the case of 1-iminopyridinium ylides, can be selectively oriented toward isomerisation or toward exocyclic N-X bond cleavage. The first process operates via an excited singlet state; the second one via a triplet state and leads to carbene, nitrene and oxene transfer reactions (See Table 7).

TABLE 7. Summary of the photochemical behaviour of pyridinium ylides 10 in benzene solution.



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REFERENCES

1. R.B. Woodward and R. Hoffmann, Die Erhaltung der Orbitalsymmetrie, Verlag Chemie, Weinheim/Bergstrasse, 1970.
2. R. Huisgen, W. Scheer and H. Huber, J. Amer. Chem. Soc., **89**, 1753 (1967)
3. M. Schultz and G. West, Angew. Chem., **82**, 265 (1970).
4. M.G. Pleiss and J.A. Moore, J. Amer. Chem. Soc., **90**, 4738 (1968).
5. J.S. Splitter and M. Calvin, J. Org. Chem., **23**, 651 (1958).
6. J. Streith, A. Blind, J.M. Cassal and C. Sigwalt, Bull. Soc. chim. France, 948 (1969).
7. R. Huisgen, Bull. Soc. chim. France, 3431 (1965).
8. R. Huisgen, Proc. Chem. Soc. (London), 357 (1961).
9. J. Streith and J.M. Cassal, C.R. Acad. Sci. Paris, **264**, 1307 (1967).
10. J. Streith and H. Strub, non published results.
11. J. Streith and J.M. Cassal, Angew. Chem. Inter. Ed. Engl., **7**, 129 (1968).
12. J. Streith and J.M. Cassal, Tetrahedron Letters, 4541 (1968).
13. K. Hafner, D. Zinser and K.L. Moritz, Tetrahedron Letters, 1733 (1964).
14. R. Gösl and A. Meuwsen, Ber., **92**, 2521 (1959); T. Okamoto, M. Hirobe, C. Mizushima and A. Osawa, Yakugaku Zasshi, **83**, 309 (1963).
15. Y. Tamura, J. Minamikawa, Y. Miki, S. Matsugashita and M. Ikeda, Tetrahedron Letters, 4133 (1972).
16. C. Reichardt, Lösungsmittel-Effekte in der Organischen Chemie, Verlag Chemie, Weinheim/Bergstrasse, p. 141-149 (1969).
17. J. Michl, E.W. Thulstrup and J.H. Eggers, J. phys. Chem., **74**, 3878 (1970).
18. R. Gleiter, D. Schmidt and J. Streith, Helv. chim. Acta, **54**, 1645 (1971).
19. J. Streith and J.M. Cassal, Bull. Soc. chim. France, 2175 (1969); A. Balasubramanian, J.M. McIntosh and V. Snieckus, J. Org. Chem., **35**, 433 (1970); T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa and K. Hayakawa, J. Org. Chem., **35**, 426 (1970); J. Streith, J.P. Luttringer and M. Nastasi, ibid., **36**, 2962 (1971).
20. A. Frankowski and J. Streith, Tetrahedron, in press (1976).
21. J. Streith and J.L. Schuppiser, unpublished results.
22. B. Willig and J. Streith, Tetrahedron Letters, 4167 (1973).
23. G. Taurand and J. Streith, Tetrahedron Letters, 3575 (1972).
24. J. Streith and G. Wolff, unpublished results.
25. J.P. Luttringer and J. Streith, Tetrahedron Letters, 4163 (1973).
26. W. Lwowski, Nitrenes, Interscience, New-York, 1970.
27. G.G. Spence, E.C. Taylor and O. Buchardt, Chem. Rev., **70**, 231 (1970).
28. F. Bellamy and J. Streith, Heterocycles, in press (1976).
29. S. Yamada, M. Ischikawa and C. Kaneko, Tetrahedron Letters, 977 (1972).
30. K.B. Tomer, N. Harrit, I. Rosenthal, O. Buchardt, P.L. Kumler and D. Creed, J. Amer. Chem. Soc., **95**, 7402 (1973).
31. J. Streith and C. Sigwalt, Bull. Soc. chim. France, 1157 (1970).
32. O. Buchardt, C.L. Pedersen and N. Harrit, J. Org. Chem., **37**, 3592 (1972).
33. R.S. Becker and M. Kasha, J. Amer. Chem. Soc., **77**, 3669 (1955); L. Pekkarinen and H. Linschitz, ibid., **82**, 2407 (1960); R. Livingston and E. Enzimoni, ibid., **80**, 5610 (1958).
34. F. Bellamy, P. Martz and J. Streith, Heterocycles, **3**, 395 (1975).