PHOTOCHEMISTRY OF PYRIDINE N-OXIDES. TRAPPING OF AN INTERMEDIATE WITH AMINES

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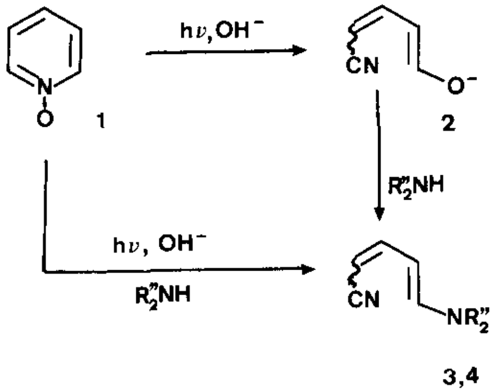
Abstract - The photochemistry of pyridine N-oxide (1a) and the corresponding 4-benzyl (1b), 4-phenyl (1c), and 2,6-dimethyl (1d) derivatives has been investigated or reinvestigated. Substrates 1a and 1b yield a small amount of the corresponding 2-acylpyrroles (5a,b) as the only isolable product, 1d yields 5d in moderate yield and 1c yield 5c in aprotic and the 2-pyridone 7c in protic solvents. In the presence of diethylamine isomeric 5-diethylaminopentadienenitriles (3,4) are obtained in moderate yield along with deoxygenated pyridines (6). Under this condition no 5 is formed, but the yield of 7 is unchanged. These reactions are most economically accounted for by admitting that nitrene 11 is formed as an intermediate and undergoes rearrangement to pyrroles 5 or polymerization to tars, or it can be trapped by amines (proton abstraction followed by nucleophilic substitution) to yield products 3 and 4. The lactams 7 arise directly from the N-oxide singlet excited state, which is also involved in the deoxygenation by amines.

The photochemistry of heterocyclic N-oxides has been extensively studied and synthetically exploited in the last thirty years.[1] A good material balance is obtained from the photolysis of these compounds, except than from a few N-oxides, notably the parent compound of the series, pyridine N-oxide, and its simple derivatives.[2] Only traces of isolable products are obtained in these cases, along with intractable "tars", although the yield of rearranged products (2-acylpyrroles) somewhat increases in the presence of copper (II) salts.[3a] Some years ago, however, Buchardt reported that pyridine N-oxide (1a) yields almost quantitatively a single compound when irradiated under basic condition (5×10^{-2} M aqueous sodium hydroxide), and this is the open-chain anion 2.[4] This product can be isolated as a salt or converted to the enaminonitriles of structure

3a and 4a (mixture of isomers) by adding an amine before or after irradiation[5] (Scheme 1).

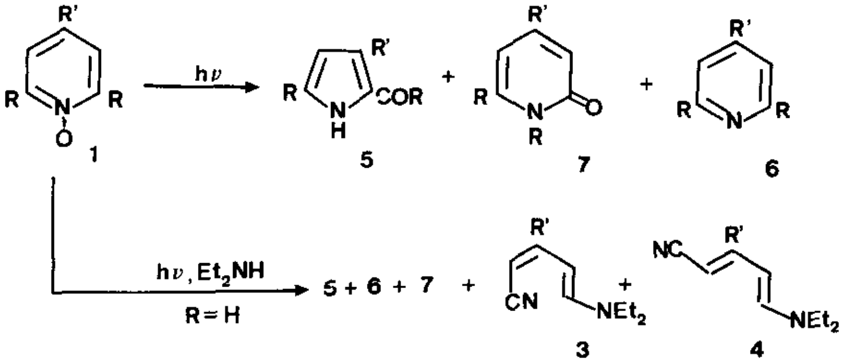


Scheme 1

As previous investigations[4] are limited to the case of pyridine *N*-oxide in water, it appeared desirable to explore the scope of the photoreaction in the presence of bases with respect both to the effect of solvents and to the effect of substituents, with the aim of obtaining a more detailed characterization of the mechanism and of testing the synthetic usefulness of this process. Besides the parent compound, 4-benzyl-, 4-phenyl, and 2,6-dimethylpyridine *N*-oxides (1b-d) were examined. In view of the previous results and the required solubility in organic solvent an amine (diethylamine) was chosen as the base. The irradiation was carried out both in the presence and in the absence of the amine in ethanol and in ethyl acetate, taken as representative protic and, respectively, aprotic solvent, in view of the known influence of proticity on the *N*-oxide photorearrangement.[1] In the case of 1a the experiments were carried out in other solvents as well.

RESULTS

Preparative Photoreactions. Irradiation of pyridine *N*-oxide (1a) in water containing 0.2 M diethylamine followed by extraction and distillation under reduced pressure yields the enaminonitriles 3a and 4a (Scheme 2, Table 1,2). These are the analogues of the products previously obtained upon irradiation of 1a in the presence of sodium hydroxide and addition of the amine.[5] The yield of distilled products is poor both in the present and previous cases, due to the low thermal stability of these compounds. Nmr of the raw extract shows a yield higher than 50%. The reaction in the presence of diethylamine can be extended to organic solvents such as ethanol, ethyl acetate or acetonitrile and products 3a and 4a are obtained in comparable yield, although it is impossible to drive the reaction to completion due to the formation of highly absorbing by-product which acts as an inner filter. The formation of nitriles 3a and 4a has been ascertained also in benzene, although in this case the main process is obviously photoaddition between benzene, which absorbs most of the light, and the amine. In every case, trace amounts of 2-formylpyrrole (5a) were obtained. It was checked that 5a is the only product recovered in some percent yield after irradiation of 1a in the absence of the amine and either distillation or chromatography.



Scheme 2 A R,R' = H
b R = H , R' = CH$_2$Ph
c R = H , R' = Ph
d R = Me, R' = H

Irradiation of 4-benzylpyridine N-oxide (1b) in either ethanol or ethyl acetate leads to 3-benzyl-2-formylpyrrole (5b) as the only isolable product in 3-5% yield. When the irradiation is carried out in the same solvents in the presence of diethylamine, the expected enaminonitriles 3b and 4b are obtained along with some 4-benzylpyridine (6b). Deoxygenation to 6b is a major process in ethyl acetate/diethylamine.

With 4-phenylpyridine N-oxide (1c) ring contraction to 2-formyl-3-phenylpyrrole (5c) takes place in a reasonable yield (27%) upon irradiation in ethyl acetate. This process is less important in ethanol, where a significant yield of 4-phenyl-2-pyridone (7c) is obtained. We notice in passing that rearrangement to the corresponding lactam is a process generally observed in good yield in the photochemistry of azanaphthalenes and azaphenanthrenes N-oxides,[1] but less important with monocyclic N-oxides (such process has been reported for some pyrazine N-oxides,[3b] and is unsignificant for pyridine N-oxide and derivatives)[1,2a]. Irradiation in the presence of diethylamine leads in both solvents to enaminonitriles 3c and 4c as main products along with some 4-phenylpyridine (6c). Under this condition the formylpyrrole 5c is not formed but the yield of the pyridone 7c in ethanol is hardly influenced.

In the case of 2,6-dimethylpyridine N-oxide (1d) rearrangement to 2-acetyl-5-methylpyrrole (5d) takes place in moderate yield. Contrary to the previous case, there is little difference between protic and aprotic solvents, nor does the addition of diethylamine cause the formation of new products or significantly depress the yield of compound 5c.

Spectroscopic Studies. Irradiation of dilute (5x10^{-5} M) solutions of pyridine N-oxide in the

Table 1. Photoproducts from the irradiation of pyridine N-oxides.

Starting Material	Substituent	Solvent	Additive	Products (% yield)[a]
1a	None	H_2O	Et_2NH,0.2M	3a (11), 4a (7)[b]
		EtOH	" . "	3a (11), 4a (6), 5a (2)
		AcOEt	" . "	3a (14), 4a (7), 5a (tr)
		MeCN	" . "	3a (16), 4a (9), 5a (tr)
		C_6H_6	" . "	3a-4a (8)
1b	4-CH_2Ph	EtOH	None	5b (3)
		EtOH	Et_2NH,0.2M	3b (15), 4b (10), 6b (2)
		AcOEt	None	5b (5)
		AcOEt	Et_2NH,0.2M	3b(9), 4b (6), 5b (tr), 6b (28)
1c	4-Ph	EtOH	None	5c (9), 7c (14)
		EtOH	Et_2NH,0.2M	3c(20), 4c (13), 6c (3), 7c (15)
		AcOEt	None	5c (27)
		AcOEt	Et_2NH,0.2M	3c (14), 4c (9), 6c(12)
1d	2,6-di Me	EtOH	None[c]	5d (25)
		AcOEt	None[c]	5d (27)

a. Isolated yield, by Kugelrohr distillation or chromatography.

b. The ratio 3 to 4 is determined on the basis of the nmr spectrum of the mixture.

c. No appreciable change in the presence of 0.2M diethylamine.

Table 2. Relevant spectroscopic data for (3-substituted) 5-diethylaminopentadienonitriles 3 and 4

		NMR[a]							
Compound	Substituent	H(2)	H(3)	H(4)	H(5)	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	IR[b]
3a	None	4.35	6.7	5.45	6.65	10.5	12	12	2210, 1620
4a	"	4.65	6.9	5.15	6.5	15	11.5	12.5	
3b	3-CH_2Ph	4.35	-	5.55	6.85	-	14	14	2210, 1620
4b	"	4.85	-	5.05	6.7	-	14	14	
3c	3-Ph	4.4	-	5.7	6.4	-	13	13	2210, 1620
4c	"	4.85	-	5.3	6.2	-	13	13	

a. In $CDCl_3$, chemical shift in δ, coupling constants in Hz.

b. Measured in film on the 3-4 mixture.

presence of diethylamine causes a regular decrease of the absorption of the starting material at 264 nm and the appearance of a new absorption attributed to the enaminonitriles at 330 nm. Isosbestic points are observed during the reaction, just as it has been reported in the case of the photolysis of 1a in aqueous NaOH[4]. Taking into account the molar absorptivity of compounds 3a and 4a, it can be concluded that conversion is essentialy quantitative, and thus the poor yield obtained in preparative experiments is to be attributed to secondary processes, probably polymerization, occurring at higher concentration and loss during distillation.

The same trend is observed on irradiation of 1a-c in diethylamine /ethanol, while formation of a new maximum is less apparent in ethyl acetate, particularly in the case of 1c, or in other less polar solvents.

In every case, in the absence of diethylamine the photoreaction is much less "clean" and a new maximum not easily recognizable. The spectral changes observed during photolysis of N-oxide 1d do not appreciably differ in the presence of diethylamine, in keeping with the results of the preparative experiments, which show no effect of the amine in this case.

Flash Photolysis Studies. Microsecond flash photolysis experiments with dilute solution of these N-oxides (2×10^{-5} M) in the presence of diethylamine revealed that formation of the enaminonitriles is a relatively slow process. A similar result is obtained for the formation of anion 2 upon photolysis of 1a in aqueous NaOH[6]. No transient or permanent change in the absorption was observed on this time scale in the absence of the amine in the range 280-600 nm.

More exactly, two different phenomena are observed in the presence of the amine, the first in the millisecond time scale, the latter in seconds. Thus e.g. by flashing 1a in ethanol diethylamine a spectrum with maximum at 320 nm is observed after 50 ms and later evolves to a different spectrum with maximum at 335 nm. The latter is obviously identical with the spectrum observed on steady state irradiation (Figure 1). The spectrum with λ_{max} 320 nm appears with pseudo first order kinetics, and experiments with an amine concentration in the range 0.1-1 M are well fitted by a second order rate constant $k=92\ M^{-1}\ s^{-1}$.

Experiments in different solvents show that the rate of appearance of the new spectrum as well as its intensity decrease with the polarity of the solvent (Table 3). The same trend is observed with substituted pyridine N-oxides 1b,c (Figure 1, Table 3), while no spectral change is observed on this time scale with N-oxide 1d.

DISCUSSION

Isolated yields of photoproducts from the irradiation of the present N-oxides in "inert" solvents are quite low. A possibility would be that this is due to secondary photodecomposition of the primary products. In order to minimize this danger, preparative irradiation was carried out by means of an intense source for a short period, but even low conversion experiments did not show a substantial increase in isolated products.

With 4-phenylpyridine N-oxide (1c) and with the 2,6-dimethyl derivative 1d the yield of the corresponding 2-acylpyrrole is however more substantial. With the first of these compounds there is also a clear solvent effect, in that the pyrrole 5c is the only product in aprotic and the pyridone

Table 3. Transients observed by flash photolysis during irradiation of pyridine N-oxides 1a-c in the presence of diethylamine.

Substrate	Solvent	λ_{max}, nm[a]	k, $M^{-1}s^{-1}$[b]	λ_{max},nm[c]
1a	H_2O	310	175	328
	EtOH	320	92	340
	AcOEt	318	76	
	C_6H_{12}	305	5	
1b	EtOH	330	94	343
	AcOEt	305	60	
1c	EtOH	335	99	345

a. Absorption maximum for the spectrum observed after 50 ms.

b. Rate for the appearance of the previous maximum.

c. Absorption maximum for the spectrum observed after several seconds.

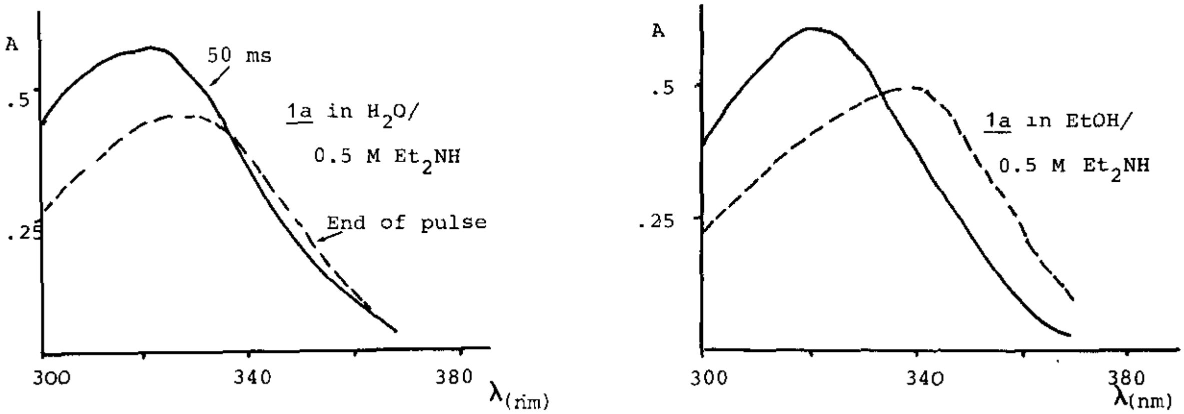
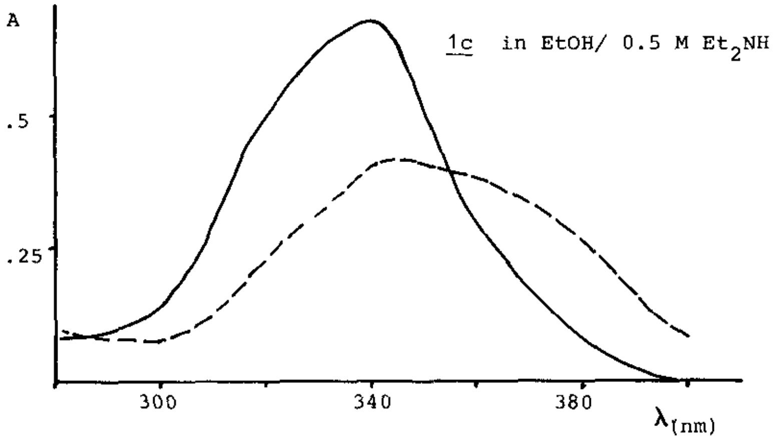


Figure 1. Spectrum observed after flashing a 10^{-5} M solution of either 1a or 1c in the presence of 0.5 M diethylamine. (———) After 50 ms. (-----) End of pulse.



6c the main product in protic solvents. This is reminiscent of what observed with other N-oxides, e.g. azanaphthalene N-oxides, where oxazepines are formed in aprotic and lactams in protic solvents, if one agrees that ring contraction to acylpyrrole is the equivalent in this case of ring enlargement to oxazepine. Oxazepines are indeed obtained from polyphenyl and dicyanopyridine N-oxides in aprotic solvents.[7]

In the presence of amines open-chain aminonitriles (3,4) are formed (provided that there is an unsubstituted α position in the pyridine ring) along with the corrisponding pyridines (6). Protic solvents favour ring cleavage, aprotic solvents deoxygenation. Under this condition the acylpyrroles are no more obtained, but the pyridone from 1c is.

In discussing the mechanism of this reaction it must first be determined which is (are) the specie(s) interacting with the amine. Although formation of ground state CT complexes between 1a and other N-oxides with aromatic amines has been documented,[8] we find no indication of a similar complex between N-oxides 1a-d and aliphatic amines (no change in the uv spectrum) nor does the quantum yield of photodecomposition of these compounds change in the presence of the amine. This latter piece of evidence as well as flash photolysis data showing that the reaction with the amine is relatively slow, allows to conclude that a reaction of an N-oxide excited state with the amine can be discarded.[§] Since furthermore the end products (the acylpyrroles 5) do not yield products 3, 4 under this condition, we are left with the hypothesis that the amine intercepts a short lived intermediate isomeric with the starting N-oxide, that otherwise rearranges to the acylpyrrole or polymerizes to intractable tars. The reaction is clearly proton abstraction, from the position and indeed does not occur when there is no α-hydrogen, as in the case of 1d. This reaction leads to anion 2 just as in the case of proton abstraction by OH^-. One can see by flash photolysis that proton abstraction by amines is ca 3 times slower than by hydroxide ion in water and becomes much slower in less protic solvent (Table 3). As for the structure of this intermediate a possibility is that rearranged compounds obtained as stable products from other N-oxides such as 1,3-oxazepines (8) or 1,2-oxazepines (9) (the latter obtained only from acridine N-oxides[9]) are formed also in this case and are much less stable. However, what is known about the reactivity of these compounds with nucleophiles (Scheme 3) does not fit with the chemistry observed in the present case. Indeed, it is known that 1,3-oxazepines undergo nucleophile addition at position 2 rather than proton abstraction.[10] Dibenzo-1,2-oxazepine undergo addition and rearrangement.[9] Benzoxaziridines 10, the products of formal electrocyclic closure, have never been actually isolated, but often postulated as intermediates in the photochemistry of N-oxides. If it is allowed to extend what is known about

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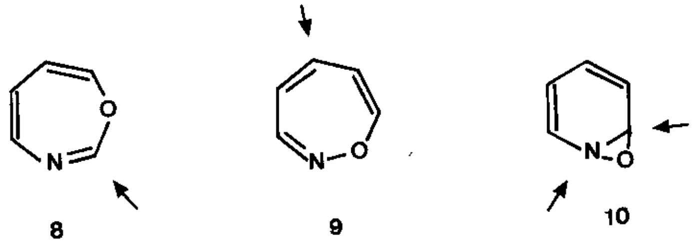
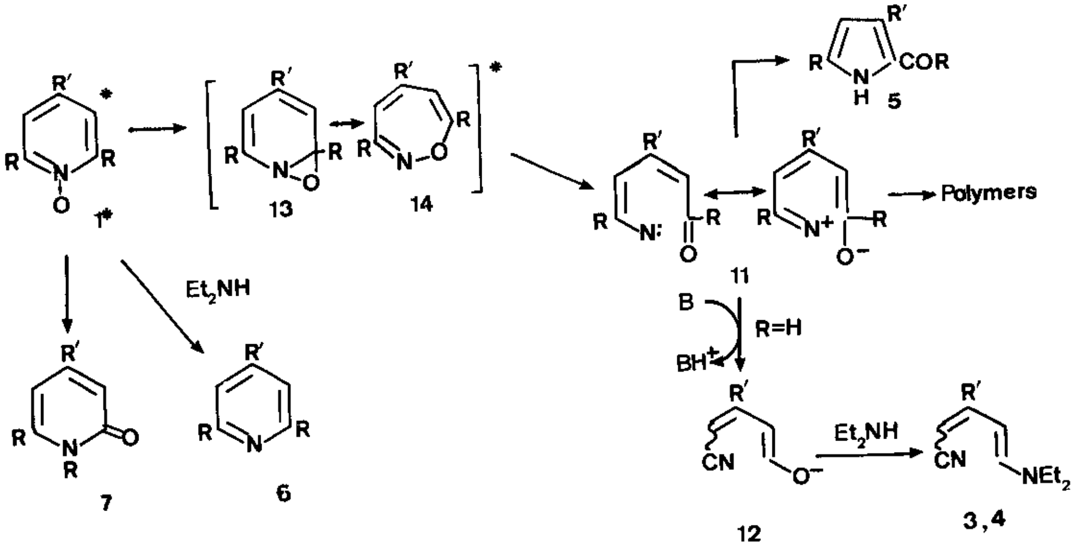
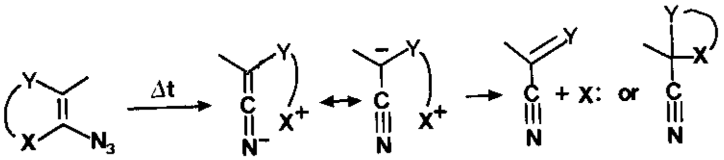
[§] At least in the case of the singlet excited state. The involvment of the triplet can also be excluded as this state ought to be detected by emission or flash photolysis, should it be that long lived as to react with bases in milliseconds. At any rate the rearrangement of heterocyclic N-oxides generally involves the singlet state, and the present pyridine derivatives do not differ in the characteristics of the photorearrangement from what observed with other N-oxides (e.g. no oxygen effect, no triplet sensitization).



Scheme 3



Scheme 4



Scheme 5

chemistry of monocyclic oxaziridines,[11] attack by nucleophiles would be possible both at carbon and at nitrogen atom, but again the expected products would not be nitriles 3 and 4.

Another intermediate which has been invoked in the photochemistry of N-oxides, and precisely with reference to the rearrangement of pyridine N-oxides to 2-acylpyrroles,[3a] is nitrene 11 (Scheme 4). In our case it can be envisaged that proton abstraction by a base leads to the conjugated anion 12 (compare Scheme 1) which in the presence of amines is the precursor of nitriles 3 and 4.

A support for this mechanism comes from literature analogy, in that vinylazides bearing in α a group capable of stabilizing a positive charge thermally decompose to nitrenes, which in turn cleave to unsatured nitriles according to Scheme 5. The relevance of nitrene-zwitterion equilibrium has been shown by trapping experiment in that case (the leaving group X^+ may be a carbonium, oxonium or iminium cation and is originally part of a ring linked to the ß-position of the azide).[12] Analogously a base promoted proton abstraction takes place in the present case on the strongly resonance stabilized nitrene 11. This might well have a lifetime in the order of milliseconds and it appears reasonable that contribution of zwitterionic mesomeric forms makes proton abstraction by bases fast enough in order to compete with intramolecular attack to yield acylpyrrole 5 and with polymerization. As expected the rate of the reaction with the base, as determined by flash photolysis, is strongly dependent on solvent polarity and scarcely influenced by substitents in position 4. The first reaction observed by flash photolysis corresponds to proton abstraction, the latter one to substitution by the amine onto anion 12 to yield 3 and 4.

Summing up, the mechanism of these reactions is shown in Scheme 4. It is apparent that the complex molecular rearrangement from singlet excited state of the N-oxide to nitrene[11] can be visualized as occurring through a sequence of steps, including oxaziridine 13 and 1,2-oxazepine 14, but to none of these stages is a significant stability associated. As it has been suggested several years ago, the entire rearrangement takes place on the excited state surface[13] and configurations such as 13 and 14 do not correspond to ground state intermediates. A funnel leading to the lowest surface is accessible only at a configuration corresponding to the nitrene, at which the $N\text{-}C_{\alpha}$ bond is already broken. The nitrene either rearranges to the corresponding 2-acylpyrrole (and metal ions stabilize the nitrene and enhance the yield of pyrroles,[3a] an example of catalysis of a photochemical reaction through stabilization of an intermediate[14]), or polymerizes or is deprotonated by bases.

Two reactions are observed, which do not involve nitrene 11. These are rearrangement to the lactam (7c from 1c) (not quenched by amines, contrary to the case of acylpyrroles (5), and directly proceeding from the excited state, reasonably the singlet[§]), and deoxygenation in the presence of amines. The latter process likely involves exothermic electron transfer from the amine to the N-oxide excited state and following oxygen transfer between the radical ions.

In conclusion pyridine N-oxide and its simple derivatives are similar to other N-oxides in that two different primary photoprocesses take place from the excited singlet state. The first

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[§] In the case of some N-oxides, it has been demonstrated that rearrangement to the lactam occurs within nanosecond.[13,15]

one, rearrangement to pyridone is of limited importance with these compounds (it becomes observable only with 1c) and is favoured, as usual, by protic solvent. *The latter one is by far the major* pathway but it leads to an unstable primary photoproducts, viz. nitrene 11. This undergoes secondary reaction to yield in negligible to moderate yield the acylpyrroles 5 and can be efficiently trapped by bases through proton abstraction, leading, when amines are used, to enaminonitriles 3 and 4. Apparently vinylnitrenes similar to those produced by thermolysis of azides[12] are obtained through a completely different way from the photochemistry of N-oxides. This *analogy suggests that the photorearrangement of pyridine N-oxides could be further exploited from* the synthetic point of view, since it yields as reactive intermediate under mild conditions.

EXPERIMENTAL

The N-oxides were prepared by standard peracid oxidation. Spectroscopic grade solvents and extra pure grade diethylamine were used as received. Uv spectra were registered on a Cary 19 spectrophotometer, ir spectra on a Perkin-Elmer 297 spectrophotometer, nmr spectra on a Brucker 80 instrument, mass spectra on Du Pont DU2 instrument, elemental analyses were carried out by means of a Carlo Erba authomatic analyzer.

Preparative Photochemical Reactions. Solutions of the N-oxides (10^{-2}M) were irradiated in an immersion well apparatus at 17°C by means of a 500 W medium pressure mercury arc. No difference was observed between nitrogen flushed and air equilibrated solutions. After that 50% or more of the starting N-oxide had reacted the irradiation was quenched and the solution was extracted by cyclohexane and benzene in the case of aqueous solutions. The solvent was then evaporated and the residue chromatographed on silica gel (Merck 0.063-0,2 mm, eluting with cyclohexane-ethyl acetate mixtures) or, in separated experiments, bulb to bulb distilled by means of a Büchi· GKR-50 instrument under reduced pressure ($< 10^{-2}$ Torr). The enaminonitriles 3-4 were obtained as a mixture and identified on the basis of elemental analysis and comparison of their spectroscopic properties (see Table 2) with previously described derivatives of similar structure.[5] The ratio of the two isomers was determined on the basis of the nmr spectrum of the mixture (see Tables 1,2).Mixture of (Z,E) and (E,E) 5-diethylaminopentadienenitrile (3a, 4a), colourless oil (bp 100°C at 0.01 mm Hg), analysis C,71.48; H,9.45; N 18.95; calculated for $C_9H_{14}N_2$: C, 71.95; H, 9.39; N,18.65 (Z,E) and (E,E) 3-benzyl-diethylaminopentadienenitrile (3b, 4b), colourless oil (bp 140°C at 0.01 mm Hg), analysis C, 79.65; H, 8.22; N, 11.60; calculated for $C_{16}H_{20}N_2$; C, 79.95; H, 8.39; N, 11.66. (Z,E) and (E,E) 5-diethylamino-3-phenylpentadienenitrile (3c, 4c) colourless oil (bp 140°C at 0.01 mg Hg), analysis C, 79.30; H. 8.15; N, 12.15; calculated for $C_{15}H_{18}H_2$: C, 79.60; H, 8.02; N, 12.38. Mass spectra of this compounds are also in accord with structure 3-Benzyl-2-formylpyrrole has nmr ($CDCl_3$) δ 9.65s, 7.3s (5H), 7.1d (J=3 Hz), 6.1d, 4.15 s; i.r. 3260, 1620 cm^{-1}. 3-Phenyl-2-formylpyrrole[3], 5-methyl-2-acetyl-pyrrole[16] and 4-phenyl-2-pyridone[17] were compared with samples obtained through known procedures.

Flash Photolysis. Flash photolysis experiments were carried out on a Applied Photophysics K-20 instrument in a cylindrical 10 cm optical path cuvette. A new solution was used for every flash. Pseudo first order kinetics were observed in every case for the amine concentration range considered (0.1-1 M).

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