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THE PHOTOCHEMISTRY OF AROMATIC N-OXIDES

A CRITICAL REVIEW

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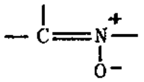
INTRODUCTION

The photochemical behaviour of aromatic-N-oxides has been explored extensively. A review article appeared in 1970 pertaining to aromatic N-oxide as well as to azoxy compound and nitrone photochemistry[1].

Aromatic N-oxides may be compared, in a formal way, to the 1,3-dipolar nitrones.



$$-\overset{|}{C}{=}\underset{\underset{O^-}{|}}{N^+}-$$

Experimentally some similarities have indeed been found:

- both types of compounds lead to 1,3-dipolar cycloaddition reactions in the ground state[2];
- both lead to atomic oxygen abstraction reactions;
- both undergo photoinduced isomerisation reactions, nitrones leading to oxaziridines, lactams or amides, whereas aromatic N-oxides yield photoisomers of various structural types.

Aromatic N-oxides have never given the corresponding oxaziridines, although these latter annelated three membered ring derivatives have been usually postulated as being the primary photoproducts.

Therefore we shall no longer compare the photochemical behaviour of aromatic N-oxides and of nitrones and focus rather upon reaction pathways of various photoexcited N-oxides all of which, in our opinion, have some common features.

1 PHOTOPHYSICAL ASPECTS

Aromatic N-oxides lead to photoproducts whose structures have been determined accurately. But when it comes to mechanistic considerations, hypotheses vary and only seldom have they been checked or disproved by physico-chemical means. To quote but one example, let us consider the determination of the transition states which are responsible for the photoisomerisation processes of pyridine-N-oxides.

In some preliminary investigations in the gas phase, it was concluded that a $\pi-\pi^*$ transition, induced by 254 nm light, was responsible for the deoxygenation whereas an $n-\pi^*$ transition, induced by 326 nm light, lead to isomer formation[3]. These results seemed to apply also to the photochemistry of pyridine-N-oxides in solution, where a hypsochromic shift is observed for the absorption band of lowest energy when the solvent polarity increases[4]. Unfortunately such a solvent dependent hypsochromic shift, although quite valid for ketones, no longer holds with pyridine-N-oxides: it could be shown that their $\pi-\pi^*$ absorption band undergoes hypsochromic shift with increasing solvent polarity[5]. This result also indicates that a π^* state is less stabilized in a polar medium than the ground π state.

In 1968 Evleth reached the conclusion that the $n-\pi^*$ transition of pyridine-N-oxide is the one which appears at highest wavelength[6]. Shortly thereafter Labhart, after a careful study of the pyridine-N-oxide absorption bands in decalin, concluded that the two transitions, which appear at λ_{max} 320 nm and 280 nm, are of the $\pi-\pi^*$ type[7]. SCF-MO calculations seemed to indicate that the lowest energy transition of pyridine-N-oxides, as observed at 3.81 eV, is indeed of the $\pi-\pi^*$ type; the probability of finding an $n-\pi^*$ transition at about 3 eV is supposed to be very small[8]. In agreement with these latter predictions it was estimated that the oscillator force ratio $f(n-\pi^*/f(\pi-\pi^*)$ is only 0.05[9].

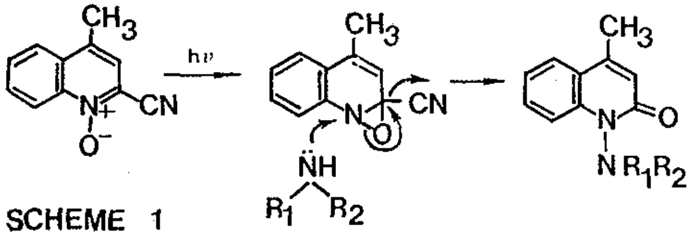
Reports about photosensitized reactions of aromatic N-oxides are equally conflicting. The study of the oxygen effect upon the photochemistry of quinoline[10]- isoquinoline[11]- and phthalazine[12]-N-oxides lead to the conclusion that an excited singlet is responsible for the deoxygenation process. On the contrary, addition of benzophenone, which absorbs more than 90% of the incident light, to a solution of 2,4,6-triphenylpyridine-N-oxide, dramatically increases deoxygenation. From this latter result it was concluded that a triplet is responsible for the deoxygenation process[13].

As far as spin multiplicity of the excited states is concerned, it is by now well established that for isoquinoline-N-oxides[14,15], pyridazine-N-oxides[16] and phthalazine-N-oxides[16], the triplet is responsible for oxygen abstraction whereas an excited singlet leads to isomerisations and rearrangements.

In order to explain the formation of the various photoisomers, it seemed straightforward to postulate oxaziridines as being the first formed intermediates. Indeed they have been put forward by almost all chemists who are active in the field of aromatic N-oxide photochemistry[1].

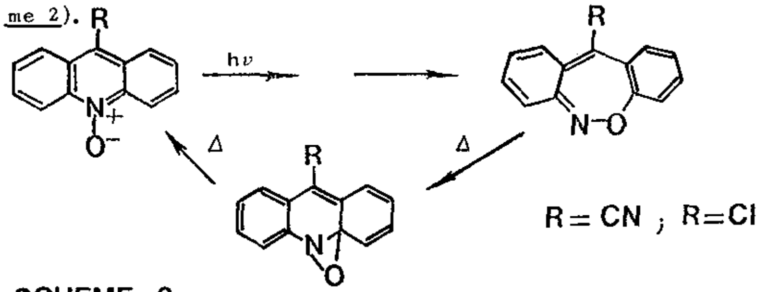
Let us quote a few facts which are more or less in favour of an oxaziridine intermediate:

a) Irradiation of 2-cyano-4-methylquinoline-N-oxide in the presence of amines leads to the corresponding N-amino-carbostyrils after expulsion of the cyano group. By analogy with the reactivity of aliphatic oxaziridines, which react with secondary amines and yield hydrazine derivatives, it was assumed that the amines react with intermediates as depicted in Scheme 1.[17]



SCHEME 1

b) UV irradiation of acridine-N-oxides leads to the corresponding dibenzooxazepines, the only known stable 1,2-oxazepines which have ever been obtained[18]. These latter ones revert back to the corresponding N-oxides by thermal activation in aprotic solvents, a process which is best explained by assuming the intermediate formation of the oxaziridine derivatives (Scheme 2).

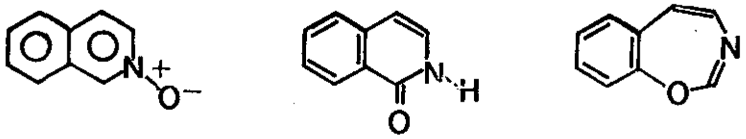


SCHEME 2

c) Various semi-empirical quantum-mechanical models have been used in order to approach the reactivity of aromatic-N-oxides (LCAO-MO; PPP-SCF; HMO)[19,20,21,22]. All these calculations arrive at a common conclusion, namely that the isomeric oxaziridines have but a minute chance to initiate from the ground state and are very likely to arise from the first excited singlet state.

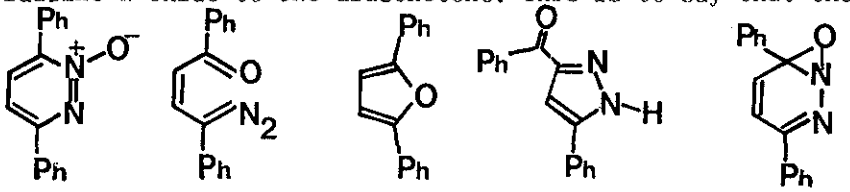
None of these experimental results and theoretical calculations are convincing evidence in favour of an oxaziridine *intermediate*, which has never been detected by any physical means. During the photoisomerisation of isoquinoline-N-oxides toward the corresponding isocarbostyriles or to the benzoxazepines, no intermediates at all have been detected, although more than one must be postulated *in order* to account for the structure of these photoproducts (Scheme 3)[14,15].

During the photolysis of 3,6-diphenylpyridazine-N-oxide, which leads to a mixture of 2,5-diphenylfuran *and of 3-benzoyl-5-*phenylpyrrazole, the unstable diazoketone has clearly been identified[16]. (Scheme 4). It has been shown, by means of nanosecond flash-photo-



SCHEME 3

lysis, that a diazoketone is the primary photoproduct i.e. that no intermediate occurs on the pathway which leads from the excited pyridazine-N-oxide to the diazoketone. This is to say that the



SCHEME 4

oxaziridine does not form at all, the geometry of the excited-state hypersurface beeing such that no minimum corresponding to the stable ground-state oxaziridine appears[16]; this latter structure is completely by-passed. Such a conclusion, which is well substantiated, may seem puzzling since the overall geometry undergoes quite a change on its pathway from the N-oxide to the diazoketone. Nevertheless it seems to fit with quanto-chemical predictions[23]. Similar conclusions have been reached by means of flash-photolyses with phenazine-N-oxides[24]. However it remains to be seen how general they are.

2 PRIMARY PHOTOPRODUCTS

Structure and distribution of the products, isolated during the photochemical treatment of aromatic N-oxides, depend on irradiation conditions and the type of solvents used. Although some of these photoproducts derive from one or several unstable intermediates, we shall simplify matters and call them primary photoproducts. Products which can be derived in separate experiments from stable intermediates shall be referred to as secondary photoproducts (see chapter 3). There are four types of primary photoproducts:

- aromatic amines which stem from a photolytic N-O bond cleavage
- isomeric δ-lactams
- 1,2-oxazepines in some very rare cases
- 1,3-oxazepines. Both 1,2- and 1,3-oxazepines occur through skeletal rearrangement of the starting N-oxides.

2-1 Aromatic Amines.

Photolytic N-O bond cleavage has been described for the first time with pyridine-N-oxide in 1961 in the gas phase: an oxygen atom is abstracted and the parent pyridine is obtained[3,25]. Such photolytic processes have been found with all aromatic-N-oxides. They seem to initiate from excited triplet states, as has been demonstrated in a few cases (see chapter 1), whereas excited singlet states seem to be responsible for the isomerisation and rearrangement processes.

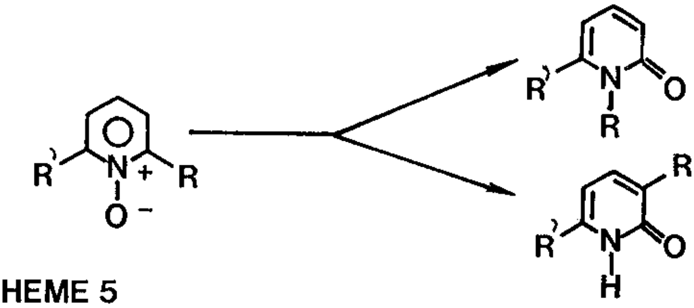
It could be shown in some series that the yield of oxygen abstraction products depends upon the wavelength of the incident light, the nature of the solvent and the pH of the reaction medium: gaseous photolysis of pyridine-N-oxide at 326 nm (87.3 Kcal/mole) and 254 nm (117 Kcal mole) leads to pyridine as the main product in both cases. However there exists a remarkable difference in the relation between the quantum yield of pyridine produced and the temperature. In the case of 326 nm irradiation the quantum yield of pyridine increases steeply at temperatures greater than 80°C, which means that an activation energy would be required for the production of pyridine. The quantum yield of pyridine produced with 254 nm irradiation is nearly independent of the temperature. These results are in good agreement with the N-O bond energy which has been estimated at 110 Kcal/mole from IR studies and dipole moment considerations[26]. Similarly in benzene solution 2,3,5,6-tetraphenylpyridine-N-oxide leads to the deoxygenated product when irradiated with UV light; but yields are quite different and again wavelength dependent (11% at 350 nm; 25% at 254 nm)[13]. The yield of oxygen abstraction products usually decreases with increasing solvent polarity. All other conditions being equal, the photochemistry of pyridine-N-oxide leads to 30% oxygen abstraction in ether and to 2% only in water [19,27]. Similar, although less pronounced effects, are observed with quinoline-[10] and phenanthridine-N-oxides[28,29,30]. In our opinion these results are quite logical since the absorption spectra of the starting material are solvent dependent (hypsochromic shift), whereas the UV lamps always have the same emission spectrum in a given set of solvent dependent experiments.

Acidity of the reaction media also plays a role as has been shown in one instance. With pyridine-N-oxide lowering of pH leads to an increase in oxygen abstraction[19]. No clearcut explanation has been put forward to account for these observations.

The question arises then as to the fate of the oxygen atoms which have been abstracted. It is doubtful that they occur as free atoms in the reaction medium. Still they are highly reactive since atomic oxygen transfer reactions — from the parent aromatic N-oxides toward solvent molecules — are observed. In benzene solution pyridine-N-oxide photolytically leads to pyridine and to phenol[31]. In a similar way pyridazine-N-oxides transfer in good yield their oxygen atom to saturated hydrocarbon solvents when excited by UV light[32]. Methylene chloride solutions of pyridazine-N-oxides in the presence of various olefins lead to photoinduced oxygen transfer whereby the corresponding epoxides are obtained[33]. The very first epoxy derivative in the aromatic series has been obtained by photoinduced atomic oxygen transfer from pyridine-N-oxide toward naphthalene, whereby 1,2-epoxy naphthalene is isolated[34]. This means that oxygen transfer may occur in two different ways: either insertion into C-H bonds or addition to double bonds. In competing reactions the insertion process is being favoured[35]. Formation of phenol with benzene probably stems from a two-step mechanism, leading first to oxepin which may then rearrange to phenol from its bicyclic valence tautomer.

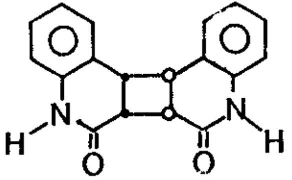
2-2 Lactams (Table1)

Photoinduced isomerisation of aromatic-N-oxides to the corresponding δ-lactams seems to be fairly general and has been observed with quinoline-, isoquinoline-, phenanthridine-, quinoxaline-, pyridine-, pyrazine-, quinazoline-,naphthiridine-, purine- and pyrimidine-N-oxides. In view of kinetic data obtained with some of the starting N-oxides[14,15] and since other photoproducts do not seem to isomerise to the corresponding lactams (for example 1,3-oxazepines do not rearrange to lactams[36]), these latter compounds are postulated as being primary photoproducts. This type of isomerisation obviously occurs through a 1,2-sigmatropic shift of the α substituent which can be a hydrogen atom (Scheme 5)

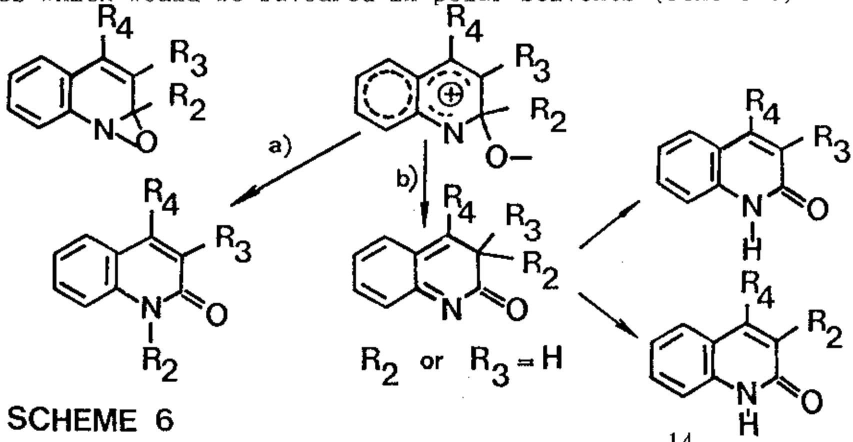


SCHEME 5

If one of the α substituents is a hydrogen atom it preferentially undergoes migration. Pyrimidine-N-oxide derivatives seem to behave in a different manner; photo-excitation of 4,6-dimethyl- and 4-phenyl-6-methylpyrimidine-N-oxides leads only to 1,6 dihydro-1,4-dimethyl-6-oxopyrimidine and 1,6-dihydro-1-methyl-4-phenyl-6-oxopyrimidine respectively[22]. Some quinoline-N-oxides lead directly to the head to head carbostyril [2+2]-dimers[37,38,39].



Lactam yields are strongly dependent upon solvent polarity and are usually higher in the more polar solvents. Therefore mechanisms which were first put forward[40,41] had to be revised in order to account for solvent polarity effects. Starting from the hypothetical oxaziridines Buchardt proposes zwitterionic intermediates which would be favoured in polar solvents (Scheme 6)[10,42,43]



SCHEME 6

More recent results, in the field of isoquinoline-[14] and phenazine-N-oxides[24] seem to be conflicting with the existence of oxaziridine intermediates. Furthermore it was shown that isocarbostyril yields are pH independent except in rather strong acidic medium of pH 3; these findings are in contradiction with zwitterionic intermediates[15].

Various primary photoisomers could originate from a common N-oxide excited state, whereby rate constants should be affected to a variable degree by solvent polarity, depending upon the isomers formed[14].

In too acidic medium quinoline-N-oxides (pH 1,5) and isoquinoline-N-oxides (pH 3.0) no longer photoisomerise to the corresponding δ-lactams, a result which is obviously due to protonation on oxygen[15,44].

Quantum yield measurements and kinetic data favour an excited singlet state as being responsible for the photoisomerisation of isoquinoline-N-oxide toward isocarbostyril[15]. In agreement with these conclusions, it was found that a lowering of pH increases the phosphorescence quantum yield and drastically reduces the isomerisation process during the excitation of quinoline-N-oxide[44].

TABLE 1 : LACTAM FORMATION

— 1 From QUINOLINE-N-OXIDES

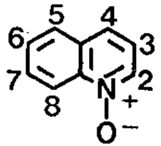
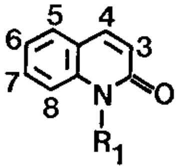
	Solvent		Yield %	References
Unsubstituted	H_2O		(55	45
			(91	10 46
	MeOH		60-70	10
	EtOH		60-70	40
	EtOH abs.		49*	10
	MeCO Me		13	45
	Et_2O		15	47
			30	10 48
R_2=Me	H_2O	R_1=Me	16	46
	H_2O	R_3=Me	10	46
	MeOH	—	22	40 41
	EtOH	—	17	46
	$C_6H_6+H_2O$	—	(low	42
	Et_2O	—	(	42
R_2=Ph	EtOH96%	R_3=Ph	8	49
	C_6H_6	—	8	36
R_2=COOH	MeOH	R_1=R_3=R_4=H	?*	50
R_3=Me	H_2O	R_3=Me	90	10 46
R_3=Et	H_2O	R_3=Et	90	10
	Me CO Me	—	17	10
R_3=Ph	EtOH	R_3=Ph	98	43
	Me CO Me	—	20	43
R_3=Br	EtOH	R_3=Br	50	10
	Me CO Me	—	57	10
R_4=Me	H_2O	R_4=M	80	10 46
	MeOH	—	70-75	41
	C_6H_6	—	42	10
	Et_2O	—	25	10
R_4= -OMe	MeOH	R_4=-OMe	60-70	41
R_4=Ph	EtOH	R_4=Ph	$\simeq$100	43
	AcEt	—	85	43
	C_6H_{12}	—	15	43
R_4=Cl	MeOH	R_4=Cl	75-80	41
	Me CO Me	—	50-70	10

TABLE 1 continued

R_4=Br	H_2O	R_4=Br	50	10
	EtOH	——	50	10
R_4=NO_2	ROH	R_4=OH	7	51
R_5=Me	H_2O	R_5=Me	88	46
R_6=Me	H_2O	R_6=Me	80	46
	EtOH	——	0*	10
	(Et_2O)	——	30	48
R_6=OMe	MeOH	R_6=OMe	50-55	41
		——	0*	10
	EtOH	——	0*	10
	C_6H_6	——	45	48
R_6=Cl	H_2O	R_6=Cl	95	10
	EtOH	——	0*	10
R_6=Br	H_2O	R_6=Br	90	10
	Me CO Me	——	39	10
R_6=F	H_2O		90	10
	Me CO Me		29*	10
R_7=CH_3	H_2O	R_7=Me	98	46
	EtOH	——	0*	10
R_7=Cl	Me CO Me	R_7=Cl	31	10
R_8=Me	H_2O	R_8=Me	80	46
	Me CO Me	——	41	10
R_8=OMe	H_2O	R_8=OMe	0*	10
R_2=R_4=Me	MeOH	R_1=R_4=Me	20	41
	MeOH	R_3=R_4=Me	15	41
	C_6H_6+H_2O	——	traces	42
R_2=Ph,R_4=Me	EtOH	R_3=Ph,R_4=Me	12	49
	PhH	—— ——	12	36
R_2=Ph,R_6=Me	EtOH 96	R_3=Ph,R_6=Me	9	49
	C_6H_6		9	36
R_4=Me, R_6=OMe	H_2O	R_4=Me,R_6=OMe	85	10
	EtOH		90	10
	C_6H_6		30	10
R_3=Me,R_4=NO_2	ROH	R_3=Me,R_4=OH	30	51

* Carbostyril dimer formation

TABLE 1 continued

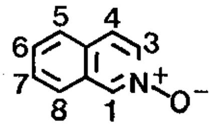
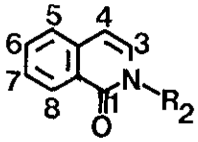
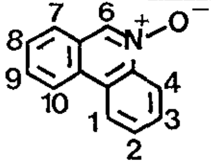
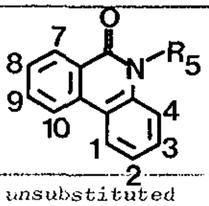
— 2	From ISOQUINOLINE-N-OXIDES			
	Solvent		Yield %	References
Unsubstituted	MeOH	unsubstituted	60-70	41 15
	EtOH		67	14
	Me CO Me		8	14
R_1=Me	MeOH	R_2=Me	35-45	41
	EtOH	———	74	14
	Me CO Me	———	< 10	14
R_1= Bz	EtOH	R_2=Bz	82	14
		———	< 10	14
R_1=PhCHMe	EtOH	R_2=PhCHMe	49	14
	Me CO Me			
R_3=Me	H_2O	R_3=Me R_2=H	95	14
	MeOH	———	65-75	41
	EtOH	———	75	14
	Me CO Me	———	26	14
	CH_2Cl_2	———	21	14
	AcOEt	———	18	14
	C_6H_6	———	6,2	14
	CCl_4	———	4,3	14
R_4=Br	EtOH	R_4=Br R_1=H	90	14
	Me CO Me	———	33	14
— 3	From PHENANTHRIDINE-N-OXIDES			
	Solvent		Yield %	References
Unsubstituted	MeOH	unsubstituted	80-85	41
R_6=Me	MeOH	R_5=Me	90	41
	EtOH	———	79; ≃100	28 30
R_6=Ph	EtOH	R_5=Ph	93; ≃100	28 30
	C_6H_6	———	16,7	29
R_6=EtCHPh	EtOH	R_5=EtCHPh		29
	C_6H_6	———		29
R_6=-CHPh$_2$	C_6H_6	R_5=-CHPh$_2$	17,2	29
R_6=O-Tolyl	EtOH	R_5=O-tolyl	high	30
	C6H6		low	30
R_6=benzhydryl	EtOH	R_5=benzhydryl		30

TABLE 1 continued

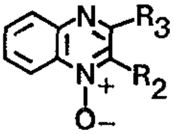
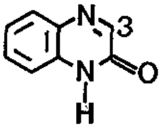
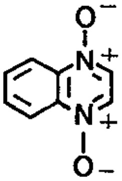
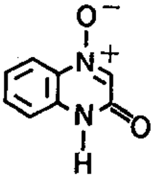
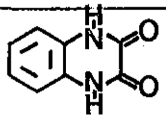
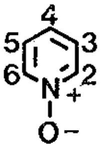
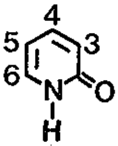
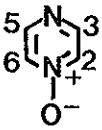
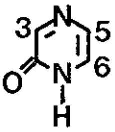
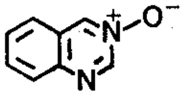
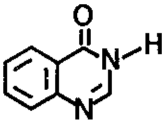
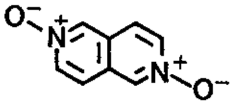
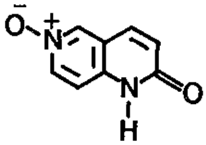
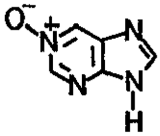
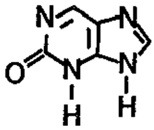
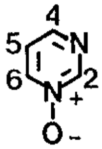
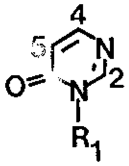
– 4	From QUINOXALINE-MONO-N-OXIDES			
	Solvent		Yield %	References
Unsubstituted	H_2O	unsubstituted	20	53
R_3=Ph R_2=H	C_6H_6	R_3=Ph	40	54
– 5	From QUINOXALINE-DI-N-OXIDES			
	H_2O		40	53
ibid.	HCl 0.5N		5	55
– 6	From PYRIDINE-N-OXIDES			
	Solvent		Yield %	References
R_2=Me R_3=R_4=R_5=R_6=H	Et_2O	R_6=Me	 1	47 27
R_3=R_5=R_6=H; R_2=R_4=Me	Et_2O	R_4=R_6=Me ; R_3=R_5=H	.8	27
– 7	From PYRAZINE-N-OXIDES			
	Solvent		Yield %	References
R_2=R_5=Me; R_3=R_6=H	H_2O	R_3=R_6=Me ; R_5=H	10	56
R_2=R_5=C_6H_5; R_3=R_6=H	C_6H_6	R_3=R_6=C_6H_5; R_5=H	3	56

TABLE I (continued)

— 8	From QUINAZOLINE-N-OXIDES			
	Solvent		Yield %	References
Unsubstituted "	EtOH C_6H_6	Unsubstituted "	80 40	57
— 9	From NAPHTHIRIDINE-DI-N-OXIDES			
	Solvent		Yield %	References
Unsubstituted	H_2O	Unsubstituted		58
— 10	From PURINE-N-OXIDES			
	Solvent		Yield %	References
Adenine-N-oxide		2-hydroxyadenine		59
Adenosine-1-N-oxide	H_2O	isoguanosine		59
6-methyl-purine-1-N-oxide		2-hydroxy-6-methyl-purine		59
— 11	From PYRIMIDINE-N-OXIDES			
	Solvent		Yield %	References
$R_4=R_6=Me$; $R_2=R_5=H$	MeOH	$R_1=R_4=Me$; $R_2=R_5=H$	13	22
$R_4=Ph$, $R_6=Me$; $R_2=R_5=H$	MeOH	$R_4=Ph$; $R_1=Me$; $R_2=R_5=H$;	10	22

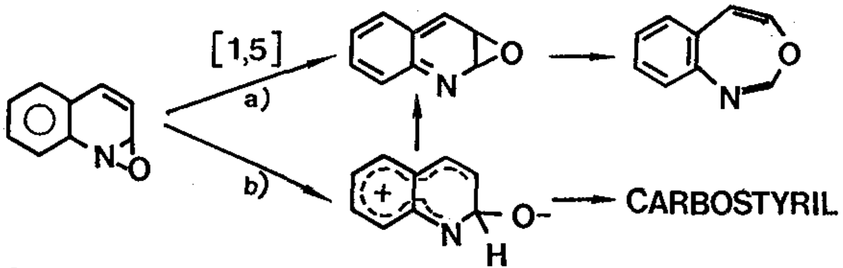
2-3 1,3-Oxazepines (Table 2)

The structure of 1,3-oxazepines, obtained for the first time by Kaneko during the UV irradiation of aromatic-N-oxides[50,54,60,61], has been established unambiguously in 1966[36,49]. 1,3-Oxazepine-photoproducts are obtained from quinoline-, isoquinoline-, pyridine-, quinoxaline-, quinazoline-, phenanthridine-, phenazine- and acridine-N-oxides.

Starting from the hypothetical oxaziridine intermediates, two different mechanistic pathways have been postulated in the first place in order to account for the formation of 1,3-oxazepines (Scheme 7)

a) via a 2,3-epoxyquinoline which is formed from the corresponding oxaziridine by a [1,5] sigmatropic shift and followed by a disrotatory valence tautomerism[43]

b) via a zwitterionic pathway which accounts simultaneously for the formation of carbostyrils and benzo-1,3-oxazepines[49,62]



SCHEME 7

Solvent polarity being without any appreciable effect upon the photoisomerisation toward 1,3-oxazepine, pathway b) has been discarded.

The last step, which has been postulated as being a valence tautomerism, seems to be well established: 1,3-oxazepines lead easily to the isomeric 3-hydroxypyridines or -quinolines, the formation of which is accounted for by an acid or base catalysed, or thermal isomerisation of the corresponding oxaziranes[61,63,64,65].

1,3-Oxazepines are not very stable compounds and lead easily by acid or base catalysis to various products which occur also during photolysis of the parent N-oxides. They can be kept in apolar and aprotic solvents and are somewhat stabilised by electron withdrawing substituents attached α to the nitrogen atom[50,61].

We believe 1,3-oxazepines to be primary photoproducts since the other photoproducts which are isolated during the photolysis of aromatic-N-oxides cannot be converted into them. Furthermore flash photolytic studies of isoquinoline-N-oxides show that they lead directly to 1,3-benzoxazepines [14].

TABLE 2 1,3-OXAZEPINES

- 1 From QUINOLINE-N-OXIDES

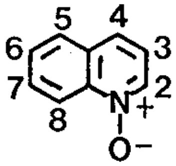
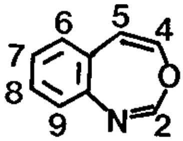
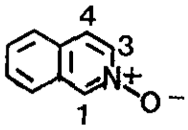
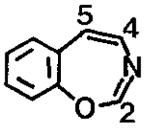
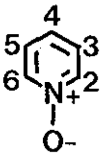
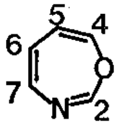
	Solvent		Yield %	References
R_2=CN	MeOH MeCOMe	R_2=CN ——	high 90	60 49
R_2=Ph	MeOH EtOH MeCOMe C_6H_6	R_2=Ph —— ——	high 78 90 61	60 49 49 36
R_2=p-Br-C_6H_4	EtOH	R_2=p-Br-C_6H_4	85	49
R_3=Ph	MeCOMe	R_4=Ph	(?)	43
R_2=CN R_3=Me	MeCOMe	R_2=CN R_4=Me	70	49
R_2=CN R_4=Me	MeOH MeCOMe	R_2=CN R_5=Me —— ——	85 90	60 49
R_2=CN R_6=Me	MeCOMe	R_2=CN R_6=Me	95	49
R_2=CN R_6=OMe	MeCOMe	R_2=CN R_6=OMe	90	49
R_2=CN R_4=Cl	C_6H_6	R_2=Cl R_5=Cl	80	50
R_2=Ph R_3=Me	MeCOMe	R_2=Ph R_4=Me	90	49
R_2=Ph R_4=Me	MeCOMe	R_2=Ph R_5=Me	90	49
R_2=Ph R_6=Me	EtOH MeCOMe C_6H_6	R_2=Ph R_6=Me —— —— —— ——	56 90 56	49 49 36
R_2=Ph R_6=Br	MeCOMe	R_2=Ph R_6=Br	65	49
R_2=p-Br-C_6H_4 R_6=Br	MeCOMe	R_2=p-BrC_6H_4 R_6=Br	80	49
R_2=CN, R_4=Me, R_6=OMe	MeCOMe	R_2=CN; R_5=Me; R_6=OMe	65	49
R_2-R_3= $(-CH_2-)_4$ R_4=H, Cl, Me, Ph, CO_2Me	C_6H_6	R_2-R_4=$(-CH_2-)_4$ R_5=H, Cl, Me, Ph, CO_2Me	unstable in the presence of moisture	66

TABLE 2 continued

— 2 From ISOQUINOLINE-N-OXIDES

	Solvent		Yield %	References
R_1=CN	CH_2Cl_2	R_2=CN	30-40	50
	MeCOMe	—	(?)	67
R_1=Ph	MeCOMe	R_2=Ph	50	67
R_1=CN R_3=Me	C_6H_6	R_2=CN R_4=Me	30-40	61
	MeCOMe	— —	?	67
R_1=Ph R_3=Me	MeCOMe	R_2=Ph R_4=Me	54	67
R_1=CN R_4=Br	MeCOMe	R_2=CN R_5=Br		68

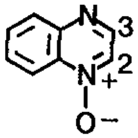
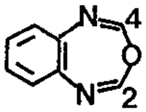
— 3 From PYRIDINE-N-OXIDES

	Solvent		Yield %	References
R_2=CN	CH_2Cl_2	R_2=CN	30	69
R_2=CN, R_4=Me	CH_2Cl_2	R_2=CN, R_5=Me	16	69
R_2=R_4=Ph	MeOH	R_2=R_5=Ph	3	13
	MeCOMe		8	13
R_2=R_3=Ph	EtOH	R_2=R_4=Ph	71-83*	64
	MeCOMe	—	76-83	64
	C_6H_6	—	55-87*	64
R_2=p-Me-C_6H_4, R_3=Ph	C_6H_6	R_2=p-Me-C_6H_4 R_4=Ph	78	64
R_2=p-Cl-C_6H_4 R_3=pH	C_6H_6	R_2=p-Cl-C_6H_4; R_4=Ph	87	64
R_2=p-Br-C_6H_4; R_3=Ph	C_6H_6	R_2=p-Br-C_6H_4 R_4=Ph	83	64
R_2=R_3=R_4=C_6H_5	C_6H_6	R_2=R_4=R_5=C_6H_5	80	64
R_2=R_3=Ph, R_4= 4-BrC_6H_4	C_6H_6	R_2=R_4=Ph, R_5 4-BrC_6H_4	76	64
R_2=R_3=R_4=R_6=Ph	C_6H_6	R_2=R_4=R_5=R_7=Ph+	30	64
		R_2=R_5=R_6=R_7=Ph unstable		64

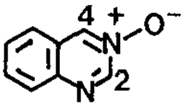
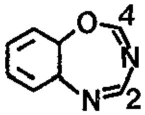
* At various wavelengths.

TABLE 2 continued

4 From QUINOXALINE-N-OXIDES

	Solvent		Yield %	References
R_2=Ph	C_6H_6 MeCOMe	R_2=Ph(unstable) ———	70	54 70 62
R_3=Ph	C_6H_6 MeCOMe	R_4=Ph(unstable) ———	45	70 62
R_2=R_3=Ph	C_6H_6 MeCOMe	R_2=R_4=Ph ———	60-70	54 62 71
R_2=R_3=p-Br-C_6H_4	MeCOMe	R_2=R_4=p-Br-C_6H_4	70	62

5 From QUINAZOLINE-N-OXIDES

	Solvent		Yield %	References
R_2=Ph	C_6H_6	R_2=Ph	83	72
R_4=Ph	C_6H_6	R_4=Ph	high	57
R_2=Me R_4=Ph	C_6H_6	R_2=Me, R_4=Ph	46	57
R_2=Me R_4=Cl	C_6H_6	R_2=Me, R_4=Cl	83	72

6 From PHENANTHRIDINE-N-OXIDES

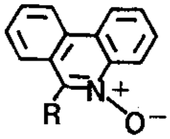
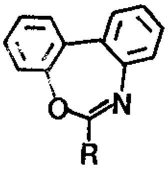
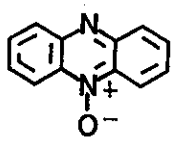
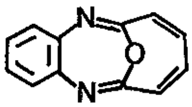
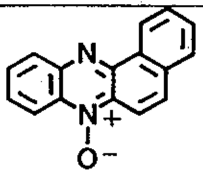
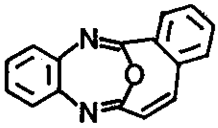
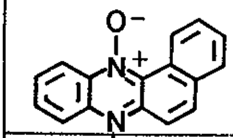
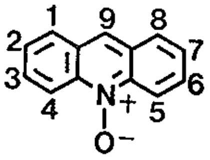
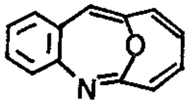
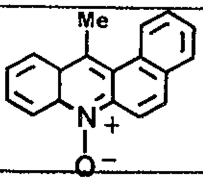
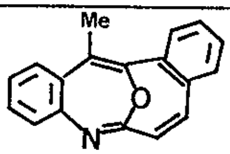
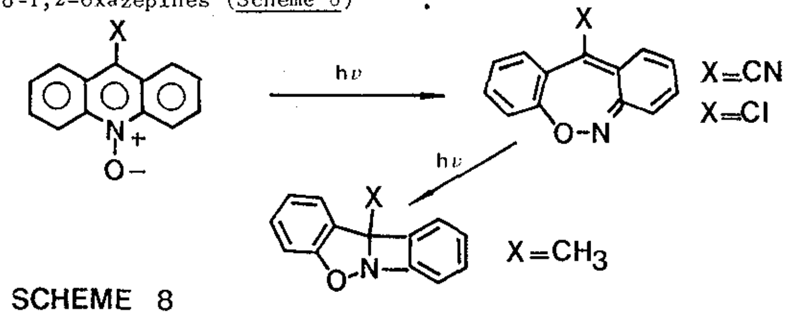
	Solvent		Yield %	References
R=Ph	C_6H_6	R=Ph	3	29
R=H	C_6H_6	R=H(unstable)		30
R=o-tolyl	C_6H_6	R=o-tolyl		30
	EtOH	R=o-tolyl		30

TABLE 2 continued

— 7	From BENZOPHENAZINE-N-OXIDES			
	Solvent		Yield %	References
	C_6H_6	unstable		73
	EtOH		75-85	74
	EtOH	idem	30	74
— 8	From ACRIDINE-N-OXIDES			
				
R_9=CN	H MeOH	R_9=CN	2-3	75 75
R_2=R_7=CH_3, R_9=CN	MeOH C_6H_6	R_2=R_7=CH_3, R_9=CN	≃1 3-5	75 75
	EtOH		80	74

2-4 1,2-Oxazepines (Table 3)

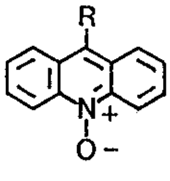
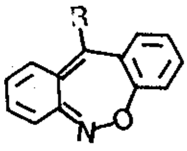
1,2-Oxazepines are unstable oxa-analogs of the known (1-H)-1,2-diazepines which can easily be obtained through UV irradiation of 1-iminopyridinium ylides[76,77,78]. The N-O bond energy compares unfavorably with the energy of the N-N bond[79] and accounts for the fact that 1,2-oxazepines could be isolated in only one instance, although they are usually postulated as intermediates in the photoinduced rearrangement of six membered aromatic N-oxides (leading to acylpyrrole derivatives). Only 10-cyano- and 10-chloroacridine-N-oxides were reported to lead to the corresponding dibenzo-1,2-oxazepines (Scheme 8)[25,80].



SCHEME 8

10-Methylacridine-N-oxide leads to a similar 1,2-oxazepine but this latter one cannot be isolated and undergoes a second photoinduced electrocyclisation to the isomeric benzisoxazoline (Scheme 8). It is reasonable to assume that 1,2-oxazepines occur as intermediates each time an aromatic N-oxide photochemically leads to a 2-acylpyrrole derivative. Recent photochemical studies performed with pyridine-N-oxides in the presence of copper II salts suggest that 2-acylpyrroles originate from 1,2-oxazepines rather than from 1,3-oxazepines[19].

TABLE 3 1,2-OXAZEPINES FROM ACRIDINE-N-OXIDES

	Solvent		Yield %	References
R = CN	C_6H_6	R = CN	59	18
R = Cl	C_6H_6	R = Cl	50	18

3 SECONDARY PHOTOPRODUCTS

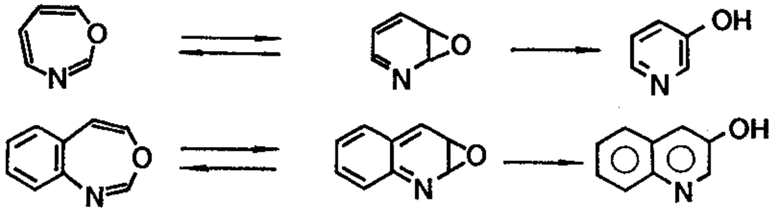
We shall discuss in this chapter the formation of reaction products which are usually obtained in two different ways:

- by direct irradiation of aromatic N-oxides (route A)
- by rearrangement of a primary photoproduct (route B)

One further point should be stressed: only 1,2- and 1,3-oxazepines lead to rearrangement products; lactams are usually stable products.

3-1 β-Hydroxypyridines and analogs (Table 4)

3-Hydroxy derivatives have been found in two series only: with pyridine- and with quinoline-N-oxides. It is reasonable to assume that 3-hydroxypyridines originate from the corresponding 2,3-epoxypyridines which are also in tautomeric equilibrium with 1,3-oxazepines (Scheme 9). Several β-hydroxypyridines are obtained via route A but only one example is known with quinoline-N-oxides[50]. This is due to the greater stability of benzo-1,3-oxazepines as compared to 1,3-oxazepines: the driving force which pushes 2,3-epoxyquinoline (non-aromatic) toward 1,3-benzoaxepine (in part aromatic) is obviously greater[81,82] than the one which leads from 2,3-epoxypyridine to 1,3-oxazepine. 1,3-Benzoxazepines and 1,3-oxazepines both isomerise via route B to the corresponding β-hydroxy derivatives.



SCHEME 9

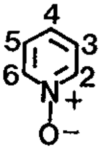
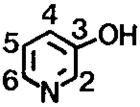
3-2 1-Acyl-2-hydroxy-2,3-dihydropyrroles (Table 5)

1-Acyl-2-hydroxy-2,3-dihydropyrrole derivatives have been isolated with pyridine- and quinoline-N-oxides. These hemiaminals may equilibrate with the isomeric open chain aminoaldehydes. Their formation is best explained by assuming hydrolytic ring opening of the 1,3-oxazepines to the amino aldehydes followed by (reversible) ring closure (Scheme 10)[36,84].

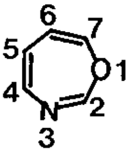
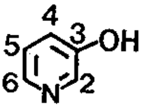
Dehydration of the hemiaminals occurs easily to the corresponding N-acylpyrroles.

TABLE 4 β-HYDROXYPYRIDINES AND ANALOGS

– 1 From PYRIDINE-N-OXIDES

	Solvent and reaction conditions		Yield %	References
R_2=Me	Et_2O Route A	R_2=Me and R_6=Me	2,5 2,5	27 31
R_2=R_4=Me	Et_2O Route A	R_2=R_4=Me and R_4=R_6=Me	3,3 6	27
R_2=R_6=Me	Et_2O C_6H_6 Route A	R_2=R_6=CH_3 ———	8 16	27 31 27
R_2=R_4=R_6=Me	Et_2O Route A	R_2=R_4=R_6=Me	21	27
R_2=R_4=R_6=Ph	MeOH Me CO Me Route A	R_2=R_4=R_6=Ph ———	38 10	13 13
R_2=R_3=R_6=Me	ET_2O Route A	R_2=R_5=R_6=Me	16	27

– 2 From 1,3-OXAZPINES

	Solvent and reaction conditions		Yield %	References
R_2=Ph	N-HCl, C_6H_6;160° Route B	R_2=Ph R_2=Ph	11 100	83 65
R_2=R_4=R_5=R_6=Ph	By column chromatography	R_2=R_4=R_5=R_6=Ph	high	64

– 3 From QUINOLINE-N-OXIDES

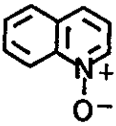
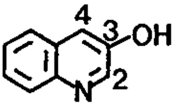
	Solvent and reaction conditions		Yield %	References
R_2=CN;R_4=OMe	C_6H_6 or CH_2Cl_2 Route A	R_2=CN; R_4=OMe	80	50 63

TABLE 4 continued

4 From 1,3-BENZOXAZEPINES

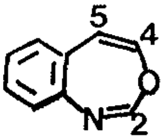
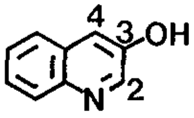
	Solvent and reaction conditions		Yield %	References
R_2=CN	CF_3COOH, 20° CH_3COCl 20° Route B	R_2=CN R_2=CN	8 60	63 84 63
R_2=CN, R_4=Me	CF_3 COOH, 20° Br_2 CH_2Cl_2 CH_3COCl, 20° Route B	R_2=CN, R_4=Me —— —— —— ——	89 56 78	61 63 84 61 63 84 67
	BCl_3 C_6H_6 Route B	R_4=CN, R_2= $CONH_2$	68	67
R_2=CN, R_4=Cl	CH_3COCl, 20°	R_2=CN, R_4=Cl	25	63 84

TABLE 5 1-ACYL-2-HYDROXY-2,3-DIHYDROPYRROLES

- 1 From QUINOLINE-N-OXIDES

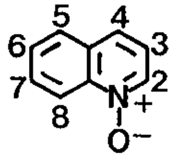
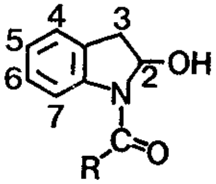
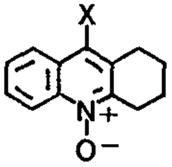
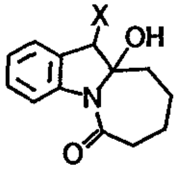
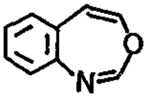
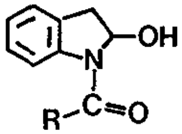
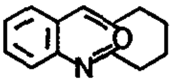
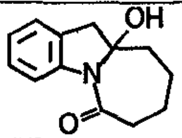
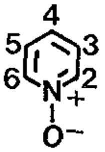
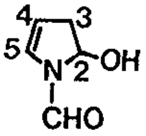
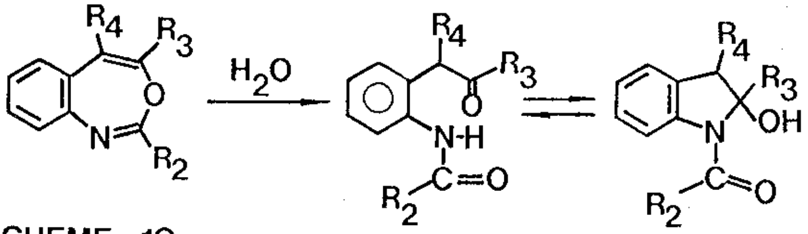
	Solvent and reaction conditions		Yield %	References
Unsubstituted	Et_2O	Unsubstituted	50	47 48
	Me CO Me	——	41	47
	C_6H_6 Route A		17	85
R_2=Me	H_2O	R=Me		86
	C_6H_6 Route A		66	84 86
R_2=Ph	C_6H_6 Route A	R=Ph	10	36
R_4=Me	C_6H_6	R_3=Me	4	10
	Et_2O	——	25	10
R_4=Ph	cyclo-C_6H_{12}	R_3=Ph	15	43
R_4=Cl	Me CO Me Route A	R_3=Cl	0-20	10
R_6=Me	Et_2O	R_5=Me	33	10 48
R_6=OMe	C_6H_6	R_5=OMe	11	10 48
R_6=Br	Me CO Me	R_5=Br	33	10
R_6=F	Me CO Me	R_5=F	45	10
	Route A	R_5=F	45	10
R_7=Cl	Me CO Me Route A	R_6=Cl	50	10
R_8=Me	Me CO Me Route A	R_7=Me	23	10
R_2=R_4=Me	C_6H_6, H_2O	R=R_3=Me	49	42
	C_6H_5	——	14	36
R_2=Ph,R_4=Me	EtOH 96% Route A	R=Ph R_3=Me	14	49
R_2=Me, R_6=OMe	Et_2O	R=Me,R_5=OMe	34	42

TABLE 5 continued

— 2	From 2,3-TETRAMETHYLENEQUINOLINE-N-OXIDES			
	Solvent and reaction conditions		Yield %	References
X=H	C_6H_6	X=H	70	66
X=Me	C_6H_6	X=Me	50	66
X=Ph	C_6H_6	X=Ph	60	66
X=Cl	C_6H_6	X=Cl	45	66
X=CO_2Me	C_6H_6 Route A	X=CO_2Me	60	66
— 3	From 1,3-BENZOXAZEPINES			
	Solvent and reaction conditions		Yield %	References
R_2=CN	dil.H_2SO_4	R=CN	?	84
R_2=Ph	EtOH,H_2O Route B	R=Ph	65	36 49
R_2=Ph; R_5=Me	EtOH,H_2O Route B	R=Ph;R_3=Me	50-60	36 49
	By column chromatography		70	70
— 4	From PYRIDINE-N-OXIDES			
	Solvent and reaction conditions		Yield %	References
R_2=Me	H_2O	R_5=Me	10	19



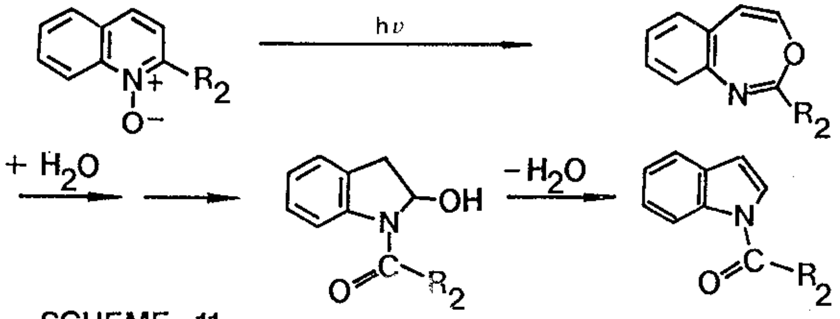
SCHEME 10

3-3 N-Acylpyrrole derivatives (Table 6)

N-Acylpyrrole derivatives, which were isolated for the first time in 1965 during the photolysis of quinaldine-N-oxide[40], are also reported to form during UV irradiation of quinoline-, pyridine-, quinazoline-, quinoxaline-, phenanthridine-, phenazine- and acridine-N-oxides. Although it was shown that 1,3-oxazepines rearrange into N-acylpyrroles, a great many mechanisms can be proposed to account for their formation.

Let us quote them briefly:

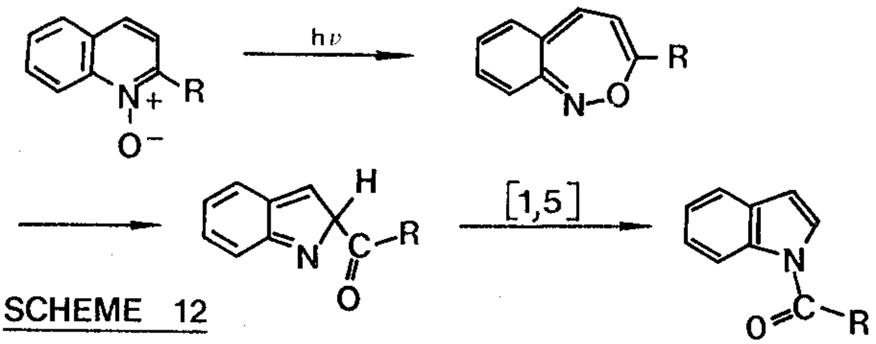
a) Thermally induced as well as acid catalysed dehydration of N-acyl-2,3-dihydro-2-hydroxypyrroles [42,10,66,87] The overall transformation of quinoline-N-oxides into N-acylindoles, as proposed by Buchardt[85], is depicted in Scheme 11. Quinoline-N-oxides, being frequently hydrated species, even irradiation in



SCHEME 11

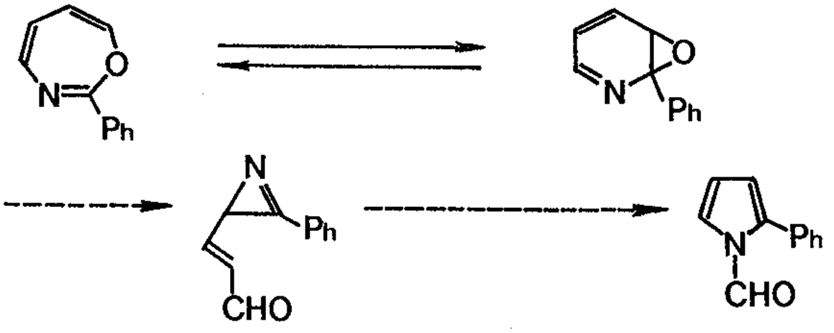
absolute ethanol leads to formation of dihydrohydroxyindoles[85].

b) The non-aromatic pyrazolenines isomerise easily to the corresponding pyrazoles by means of [1,5]sigmatropies by analogy with pyrazolenines[88] and 5,5-disubstituted cyclopentadienes; in these latter series it was shown that a formyl group undergoes [1,5]sigmatropic shift 100 times faster than hydrogen[89]. Applied to the quinoline-N-oxide series such a mechanism would be as shown in Scheme 12.



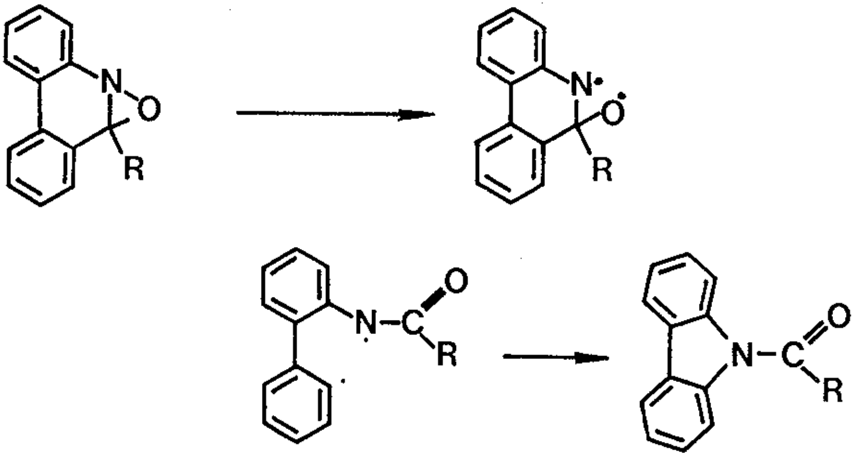
SCHEME 12

c) Valence tautomerism of 1,3-oxazepines followed by a complex ring contraction to aziridine and two consecutive [1,3]sigmatropic shifts[90] (Scheme 13). Such a mechanism would seem unlikely with quinoline-N-oxides and polycyclic aromatic N-oxides.



SCHEME 13

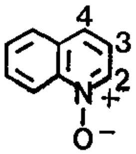
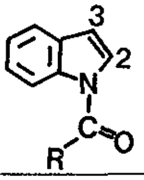
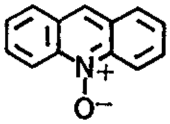
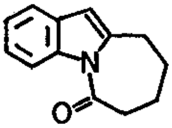
d) Taylor and Spence proposed a radical type mechanism in the phenanthridine-N-oxide series, assuming the oxaziridine as the primary photoproduct (Scheme 14)[29].



SCHEME 14

TABLE 6 N-ACYLPYRROLESPYRAZOLES and -IMIDAZOLES

– 1 From QUINOLINE-N-OXIDES

	Solvent and reaction conditions		Yield %	References
Unsubstituted	MeOH	Unsubstituted	2.5	41
	Me CO Me	R=H	3	87
	Et_2O	-	2-5	85
	abs. EtOH	-	1	85
	C_6H_6 Route A	-	16	85
R_2=Me	CH_3OH	R=Me	10	40 41
	C_6H_6 Route A	-	low	86
R_2=R_4=Me	C_6H_6, H_2O Route A	R=R_3=Me	low	42
	MeOH EtOH Route A		10	66

– 2 From N-ACYL-INDOLINOLS

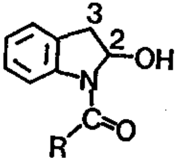
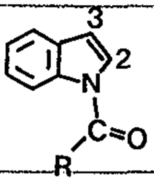
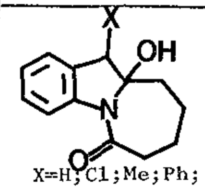
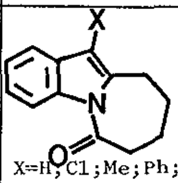
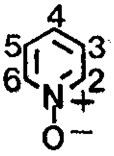
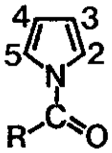
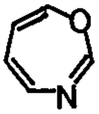
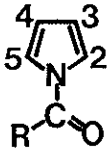
	Solvent and reaction conditions		Yield %	References
R=Me	P_2O_5, 165°	R=Me	100	42
	0.4 N HCl; 80° Route B	"	5	42 86
Unsubstituted	anhydrous HCl reflux in $CHCl_3$ Route B	unsubstituted	?	87
 X=H; Cl; Me; Ph; CO_2Me	Heating or in acid medium 20° Route B	 X=H; Cl; Me; Ph; CO_2Me	85-95	66

TABLE 6 continued

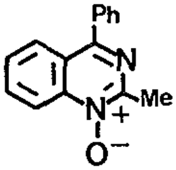
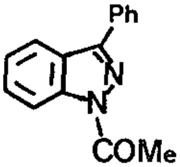
– 3 From PYRIDINE-N-OXIDES

	Solvent and reaction conditions		Yield %	References
Unsubstituted	MeOH	Unsubstituted	Low	101
	EtOH Route A	R = H	Low	101
R_2=$CONH_2$	H_2O Route A	R=H; R_2=$CONH_2$	22	91

– 4 From 1,3-OXAZEPINES

	Solvent and reaction conditions		Yield %	References
R_2=Ph	HCl 20°	R=Ph and	48	83
	C_6H_6, 450° Route B	R_2=Ph	14	90
'R_2=R_4=R_5=R_7 = Ph	2N HCl 20° Route B	R=R_2=R_3=R_5 = Ph	58	95

– 5 From QUINAZOLINE-N-OXIDES

	C_6H_6 Route A		30%	72

– 6 From 2-OXA(1,4)-BENZODIAZEPINES

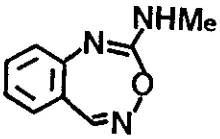
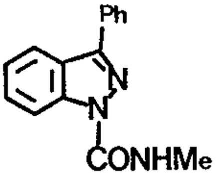
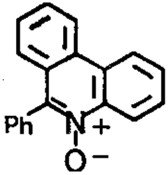
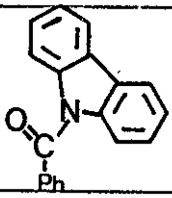
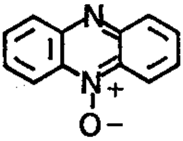
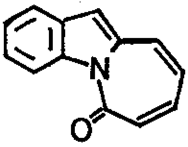
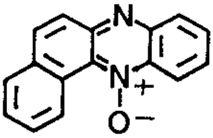
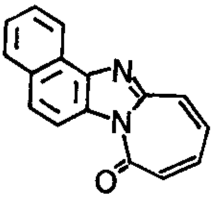
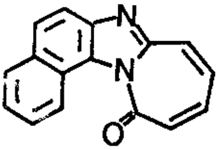
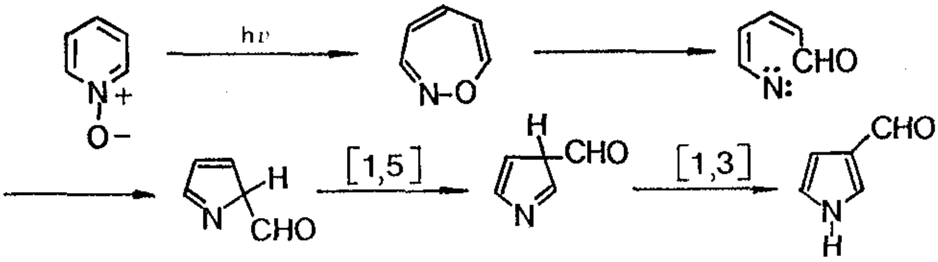
	Route A		?	130

TABLE 6 continued

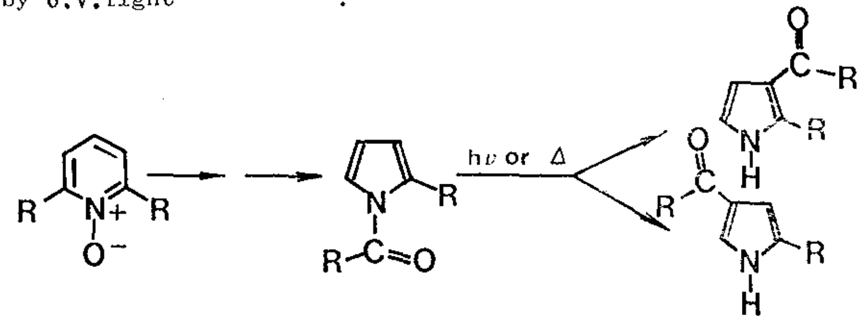
– 7	From PHENANTHRIDINE-N-OXIDES			
	C_6H_6 Route A		1%	29 30
– 8	From PHENAZINE-N-OXIDES			
	Solvent and reaction conditions		Yield %	References
–	MeOH; N_2		3	73
–	C_6H_6; N_2		38	73
–	MeOH; O_2		12	73
–	C_6H_6; O_2		42	73
–	CH_3CN Route A		51	24
	EtOH	 	25 20	74

3-4 3-Acylpyrroles. (Table 7)

3-Acylpyrroles are formed during the photolysis of quinoline-, pyridine-, pyrimidine-, phenazine-, and acridine-N-oxides and are usually thought as being formed from 1,3-oxazepines. In ouropinion *3-acylpyrroles can be formed according to mechanistic* Scheme 15 which accounts for example for the formation of 2-methyl-3-formylpyrrole during the photolysis of 3-methylpyridine-N-oxide[19]. Unfortunately such a straightforward mechanism cannot explain the formation of all 3-acylpyrroles[27]; therefore other mechanistic pathways await to be proposed, for example the one depicted in Scheme 16 which would proceed via an N-acylpyrrole and a well documented double [1,3]sigmatropic shift induced thermally or by U.V.light[90,92,93,94].



SCHEME 15



SCHEME 16

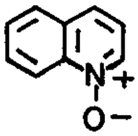
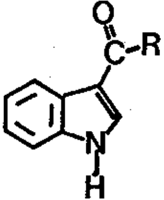
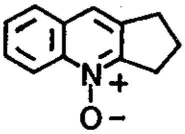
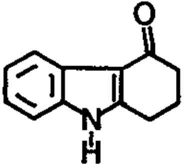
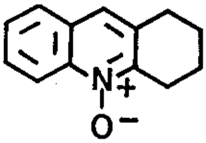
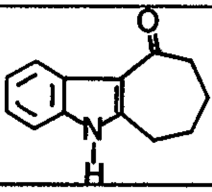
3-5 2-Acylpyrroles (Table 8)

Although 2-acylpyrroles have never been obtained according to type B reaction pathway we believe that they occur from 1,2-oxazepines. The following N-oxides lead to 2-acylpyrrole derivatives: pyridine-, pyrazine-, pyridazine-, pyrimidine- and acridine-N-oxides. *Several mechanisms have been proposed* in order to account for the formation of 2-acylpyrroles:

a) It has been postulated a simultaneous homolytic cleavage of two bonds in the oxaziridine intermediate which leads to an open chain nitrene. Intramolecular cyclisation of the latter one gives a pyrrolenine and eventually, by means of a [1,5]

TABLE 7 3-ACYL PYRROLES

– 1 From QUINOLINE-N-OXIDES via Route A

	Solvent and reaction conditions		Yield %	References
Unsubstituted	EtOH	R=H	2-4	85
	ROH C_6H_6 CH_2Cl_2		60 70 80	66 66 70
	C_6H_6		10	66

– 2 From 1,3-BENZOXAZEPINES via Route B

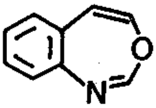
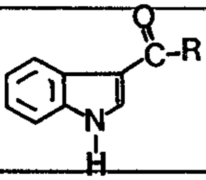
	Solvent and reaction conditions		Yield %	References
$R_2=C_6H_5$	abs. EtOH reflux	$R_2=C_6H_5$;R=H	60	43
$R_4=C_6H_5$	EtOH 70% 20°	R $=C_6H_5$	30	43
	abs. EtOH reflux	R $=C_6H_5$	100	43
$R_2=C_6H_5$;R_4=Me	abs. EtOH reflux	$R_2=C_6H_5$ R = Me	67	43

TABLE 7 continued

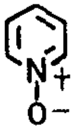
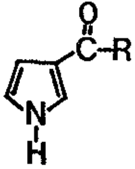
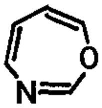
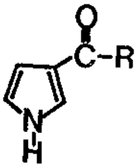
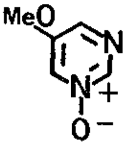
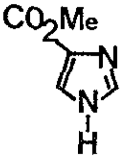
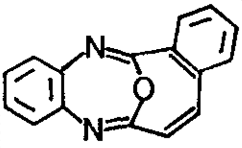
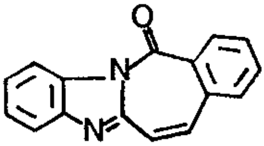
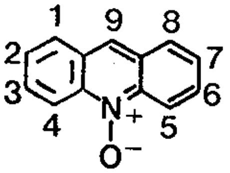
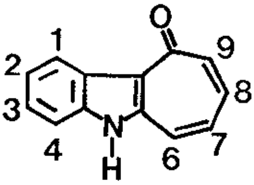
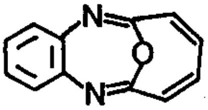
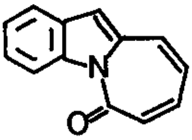
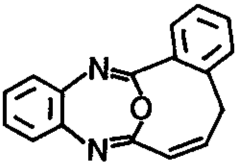
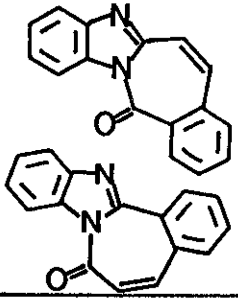
— 3	From PYRIDINE-N-OXIDES via Route A			
	Solvent and reaction conditions		Yield %	References
R_3=Me R_2=R_6=Me R_2=R_3=R_6=Me	H_2O Et_2O Et_2O	R=Me R=R_2=Me + R=R_5=Me R_2=R_3=R_5=Me	1 7 4 10	19 27 27 27
— 4	From 1,3-OXAZEPINES via Route B			
	Solvent and reaction conditions		Yield %	References
R_2=C_6H_5	C_6H_6, heat	R=H R_2=C_6H_5 + R=H R_5=C_6H_5	5 11	90 90
R_2=R_4=R_5=R_7= C_6H_5	neat, 240° 2N HCl, EtOH 2N NaOH,EtOH	R=R_2=R_4=R_5 =C_6H_5	96 21 84	95 95 95
— 5	From PYRIMIDINE-N-OXIDES via Route A			
	Solvent C_6H_6		34	96
— 6	From ANNULATED 1,3,6-OXADIAZEPINES via Route B			
	Solvent CF_3COOH		Yield 80	Reference 74

TABLE 7 continued

– 7	From ACRIDINE-N-OXIDES via Route A			
	Solvent		Yield %	References
Unsubstituted	CH_2Cl_2	unsubstituted	70-80	97
$R_2=R_7=Me$	MeOH	$R_2=R_7=Me$	2	98
	C_6H_5		13	98

– 8	From ANNULATED 3-OXA-1,5-DIAZEPINES			
	MeOH Heating Route B		low yield	73
	CF_3COOH Route B		80 5	74

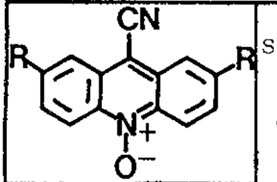
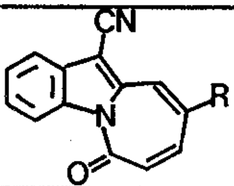
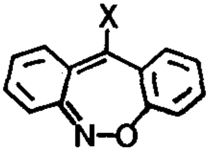
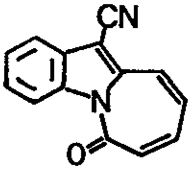
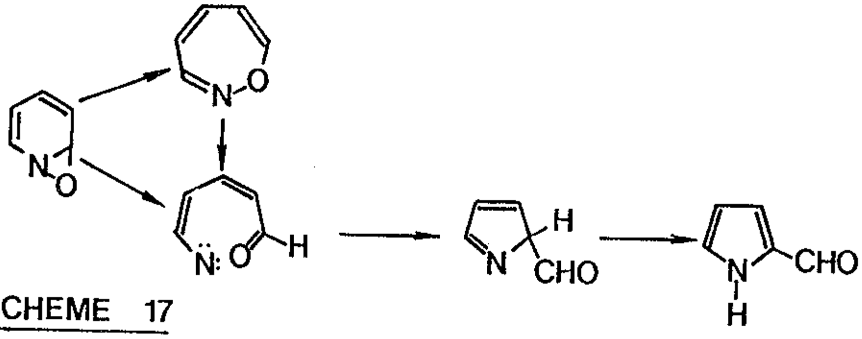
– 9	From ACRIDINE-N-OXIDES			
	Solvent and reaction conditions		Yield %	References
R=H	MeOH	R=H	low	75
	C_6H_6 Route A	–	10	75
R=Me	MeOH	R=Me	2	34 75
	C_6H_6 Route A	–	5	34 75

TABLE 7 continued

– 10 From ANNULATED 1,2-OXAZEPINES

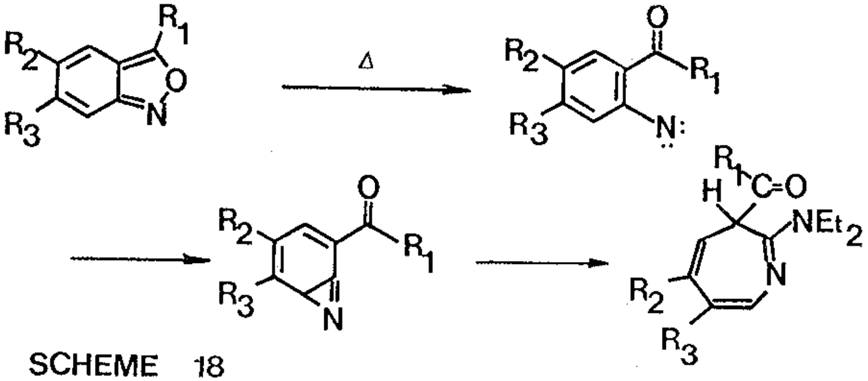
 X=Cl;CN	Column chromatography Route B	 X=Cl; CN	*3*	*73*

sigmatropic hydrogen shift, the 2-acylpyrrole (Scheme 17)[22,43]



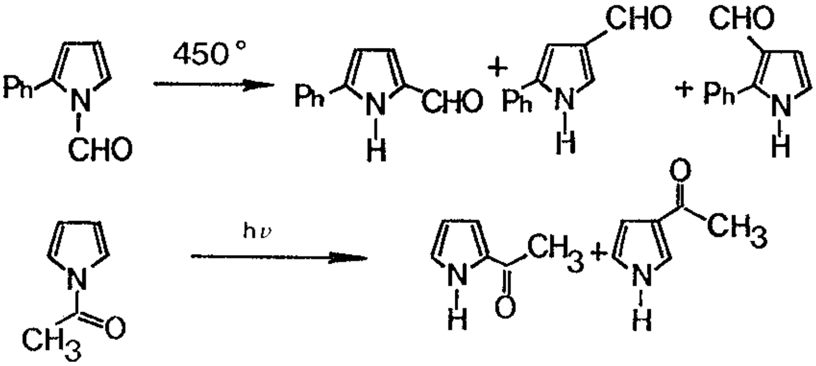
SCHEME 17

b) Homolytic nitrogen-oxygen bond cleavage occurs at the 1,2-oxazepine stage leading then to the same type of nitrene which we have encountered above. We favour this latter mechanism since similar results have been found with anthranils which open up thermally leading to [3-H]-azepines via an ortho benzoylnitrene (Scheme 18)[99,100].



SCHEME 18

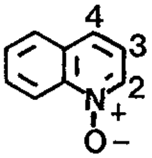
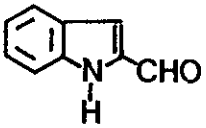
c) As a second alternative, 2-acylpyrroles could also be formed starting with N-acylpyrroles since these compounds rearrange photochemically as well as thermally to a mixture of 2- and 3-acylpyrroles [90,94] (Scheme 19). We do not favour mechanism c)



SCHEME 19

TABLE 8 2-ACYL-PYRROLES

— 1 From QUINOLINE-N-OXIDES

	Solvent		Yield %	References
$R_4=C_6H_5$	C_6H_{12}	$R_3=C_6H_5$	45	43

— 2 From PYRIDINE-N-OXIDES

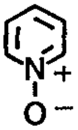
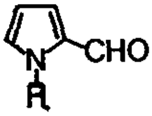
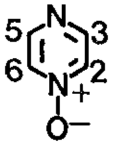
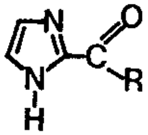
	Solvent and reaction conditions		Yield %	References
unsubstituted	H_2O	R=H	2	19
"	ROH	R=H	2	101
"	Et_2O	R=H	10	47
R_2=Me	H_2O	R=Me	< 1	19
	–	R=H; R_5=Me	< 1	19
R_2=Me	Et_2O	R=H; R_5=Me	6	27 47
R_2=OMe	H_2O	R=H; R_5=OMe	3	19
$R_2=C_6H_5$	H_2O	$R=C_6H_5$	1	19
	Me CO Me	R=H; $R_5=C_6H_5$	25	1
R_3=Me	H_2O	R=H; R_4=Me	3	19
R_3=CN	H_2O	R=H; R_4=CN	< 1	19
R_3=Cl	H_2O	R=H; R_4=Cl	< 1	19
R_4=Me	H_2O Et_2O	R=H; R_3=Me – –	1,5 3	19 27
R_4=OMe	H_2O	R=H; R_3=OMe	12	19
$R_4=OCH_2C_6H_5$	H_2O	R=H; $R_3=OCH_2C_6H_5$	4.5	19
$R_4=C_6H_5$	H_2O	R=H; $R_3=C_6H_5$	6	19
R_4=CN	H_2O	R=H; R_3=CN	4	19
R_4=Cl	H_2O	R=H; R_3=Cl	1.5	19
$R_2=R_4$=Me	Et_2O	R=H; $R_3=R_3$=Me	21	27
$R_2=R_6$=Me	C_6H_6	R=H; R_5=Me	5	27
	Et_2O	– –	9	27
$R_2=R_6$=CN	CH_2Cl_2	R=H; R_5=CN	40	69
$R_2=R_3=R_6$=Me	Et_2O	$R=R_4=R_5$=Me	10	27

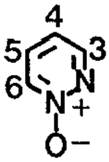
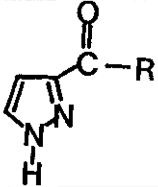
TABLE 8 continued

$R_2=R_4=R_6=Me$	Et_2O	$R=R_3=R_5=Me$	15	27
$R_2=R_4=R_6=C_6H_5$	MeOH Me CO Me	$R=R_3=R_5=C_6H_5$	37 56	13 13
$R_2=R_6=CN;R_4Me$	CH_2Cl_2+ MeOH reflux	$R=OMe;R_3=Me;R_5=CN$	29	69

— 3 From PYRAZINE-N-OXIDES

	Solvent		Yield %	References
$R_2=R_5=Me$	C_6H_6	$R=R_4=Me$	5	56
$R_2=R_5=C_6H_5$	C_6H_6	$R=R_4=C_6H_5$	15	56

— 4 From PYRIDAZINE-N-OXIDES

	Solvent		Yield %	References
$R_3=Cl;R_6=Me$	MeOH	$R=Me;R_5=Cl$	< 1	102
$R_3=OMe;R_6=Me$	MeOH	$R=Me;R_5=OMe$	< 1	102
$R_3=R_6=C_6H_5$	Me CO Me	$R=R_5=C_6H_5$	50	16 103

— 5 From PYRIMIDINE-N-OXIDES

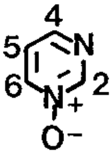
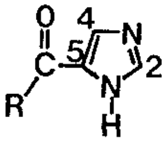
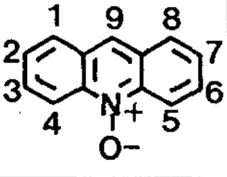
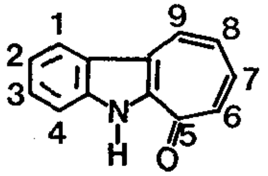
	Solvent		Yield %	References
$R_2=Me$	C_6H_6	$R=H;R_2=Me$	5	21
$R_2=OMe$	CH_3CN	$R=H;R_2=OMe$	9	96
$R_4=R_6=Me$	MeOH	$R=Me;R_2=Me$	28	22
$R_4=C_6H_5;R_6=Me$	MeOH	$R=Me;R_4=C_6H_5$	17	22

TABLE 8 continued

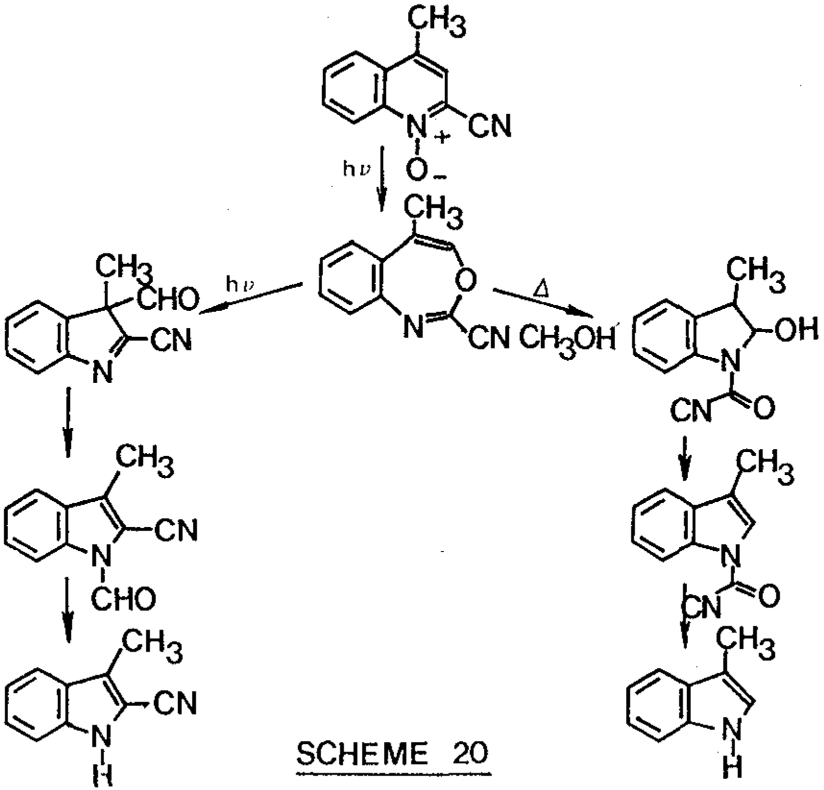
— 6 From ACRIDINE-N-OXIDES

	Solvent		Yield %	References
$R_2=R_7=Me$	MeOH C_6H_6	$R_2=R_8=Me$ -	< 1 40	98 98

in view of the fact that UV irradiation of 4-substituted pyridine-N-oxides leads to 2-formyl-pyrroles and not at all to 3-formyl-pyrroles[19].

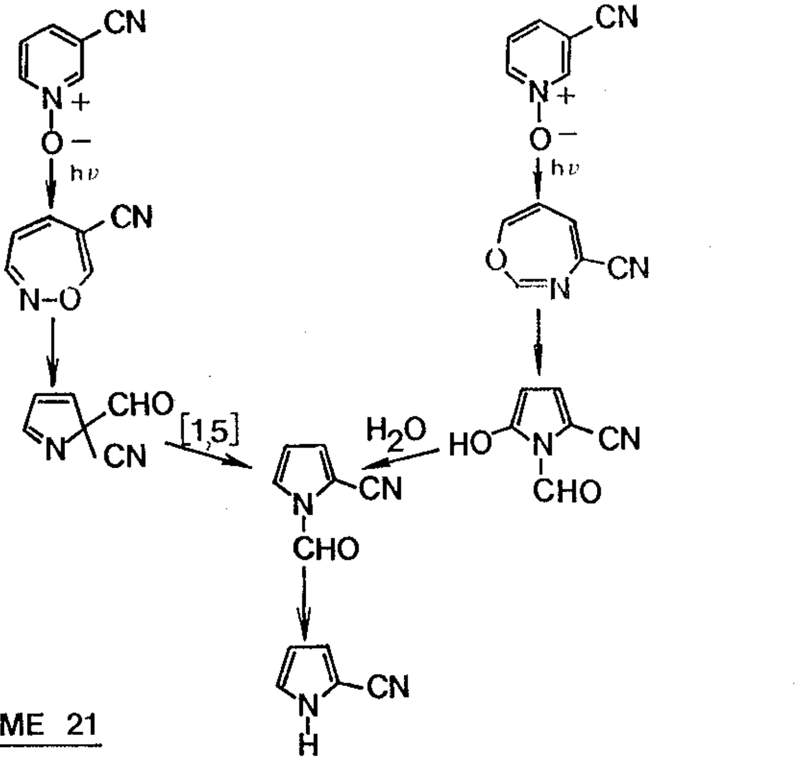
3-6 Non carbonylated Pyrrole derivatives (Table 9)

Pyrrole derivatives, whose formation is observed during the photolysis of quinoline-, pyridine-, pyrazine- and cinnoline-N-oxides, may occur from 1,3-oxazepines via N-acylpyrroles or from 1,2-oxazepines via pyrrolenines and N-acylpyrroles. These latter compounds are known to hydrolyse easily with acid or base to the corresponding pyrroles[104]. Simultaneous formation of 2-cyano-3-methylindole and 3-methylindole during the photolysis of 2-cyano-4-methylquinoline-N-oxide is best explained by the mechanistic pathways as depicted in Scheme 20 [60].



SCHEME 20

2-Cyano- and 3-cyanopyridine-N-oxide both lead photochemically in water solution to 2-cyanopyrrole, a result which is best accounted for by assuming 1,2-oxazepine and 1,3-oxazepine respectively as intermediates[19] (Scheme 21).



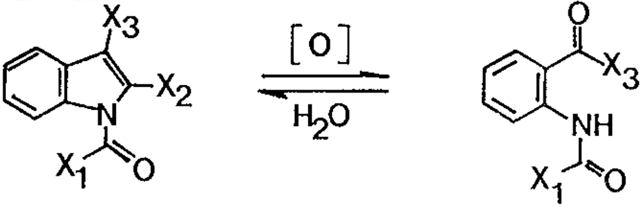
SCHEME 21

3-7 Openchain photoproducts

Openchain photoproducts are very likely to occur via 1,3- and 1,2-oxazepines.

3-7-1 From quinoline-N-oxides

We have already seen the thermal equilibrium between cyclic hemiaminals and the corresponding keto-amides. In some rare cases N-acylindoles are also oxidized in the presence of air, for example to ortho-amidophenones (Scheme 22) when substituted quinoline-N-oxides are irradiated[10,42]



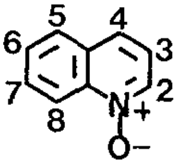
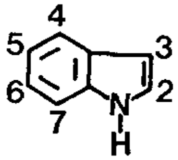
SCHEME 22

3-7-2 From isoquinoline-N-oxides

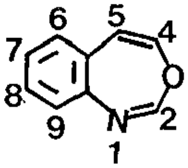
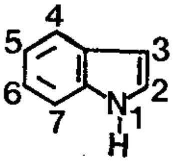
Benzo[f]-1,3-oxazepines, which are being formed during photolysis of isoquinoline-N-oxides, are hydrolysed to the corresponding conjugated amidophenols (Scheme 23) which cannot recyclise[67,68,105].

TABLE 9 NON CARBONYLATED PYRROLES

- 1 From QUINOLINE-N-OXIDES via Route A

	Solvent		Yield %	References
Unsubstituted	EtOH	Unsubstituted	1-6	85
-	Et_2O	-	20-40	85
-	C_6H_6	-	5	85
R_4=Me	MeOH	R_3=Me	5	41 42
-	Et_2O	-	<1	10
-	C_6H_6	-	10	10
R_2R_4=Me	MeOH	R_3=Me	6	41
	C_6H_6	"	29	42

- 2 From 1,3-BENZOXAZEPINES via Route B

	Solvent and reaction conditions		Yield %	References
$R_2=C_6H_5$	MeOH reflux	$R_2=C_6H_5$	12	84
R_2=CN; $R_5=C_6H_5$	MeOH, H_2O reflux	$R_3=C_6H_5$	50	60
" "	dil. H_2SO_4	"	80	63
	MeOH; hν	-	100	60

- 3 From PYRIDINE-N-OXIDES via Route A

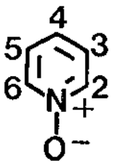
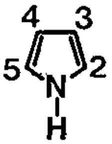
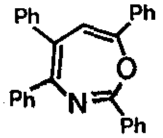
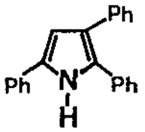
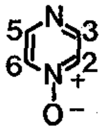
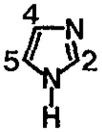
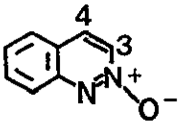
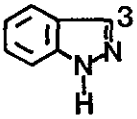
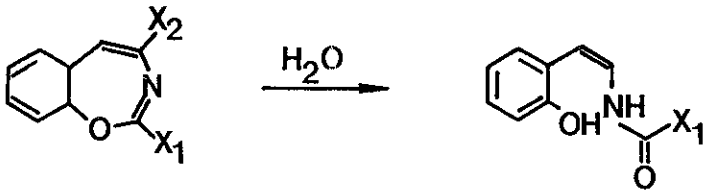
	Solvent		Yield %	References
R_2=CN	H_2O	R_2=CN	3	19
R_3=CN	H_2O	R_2=CN	1	19
R_3=Cl	H_2O	R_3=Cl	10	19

TABLE 9 continued

– 4	From 1,3-OXAZEPINES via Route B			
	2N HCl EtOH		Yield 18%	95
– 5	From PYRAZINE-N-OXIDES via Route A			
	Solvent		Yield %	References
$R_2=R_5=Me$	C_6H_6	$R_2=R_5=Me$	15	56
$R_2=R_5=C_6H_5$	C_6H_6	$R_2=R_5=C_6H_5$	29	56
– 6	From CINNOLINE-N-OXIDES via Route A			
	Solvent		Yield %	References
$R_4=Me$	MeOH	$R_3=Me$	25	105
–	C_6H_6	$R_3=Me$	25	105



SCHEME 23

3-7-3 From Phenanthridine-N-oxides.

Photoproducts which are isolated during phenanthridine-N-oxide photochemistry are analogous to the ones described with isoquinoline-N-oxides[29,30] (Scheme 24) .

SCHEME 24

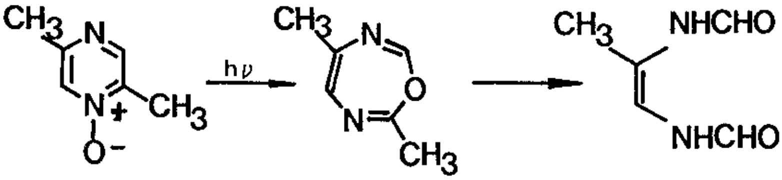
3-7-4 From quinoxaline-N-oxides.

UV excitation of 3-phenylquinoxaline-N-oxide leads to N-formyl-N'-benzoyl-o-phenylenediamine, a compound which is also obtained via hydrolysis of the corresponding benzoxadiazepine[60] (Scheme 25).

SCHEME 25

3-7-5 From pyrazine-N-oxides.

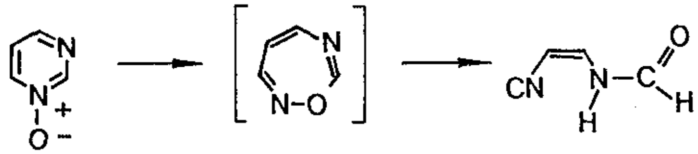
Here once more an open-chain and conjugated diamide is being obtained, probably via a 1,3,6-oxadiazepine which cannot be isolated [56] (Scheme 26) .



SCHEME 26

3-7-6 From pyrimidine-N-oxides.

U.V. irradiation of pyrimidine-N-oxides leads to open-chain conjugated nitriles, the cyano and amide functions being usually in a cis configuration[21,96,107]. 1,2,6-Oxadiazepines are believed to be the mechanistic intermediates which then open up by base catalysis (Scheme 27).

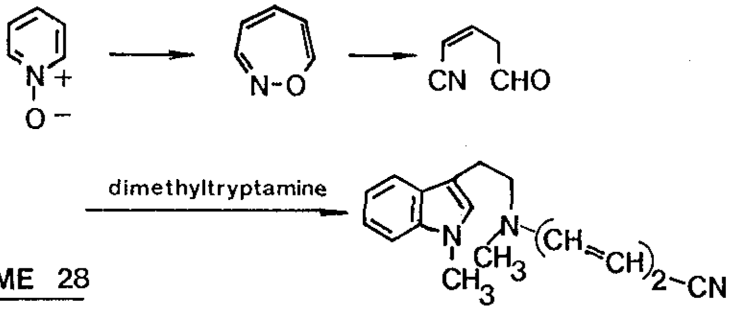


SCHEME 27

3-7-7 From Pyridine-N-oxides.

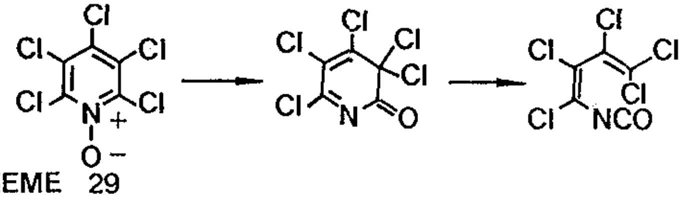
Two classes of open-chain compounds have been described during pyridine-N-oxide photochemistry:

- pyridine-N-oxide itself, when excited in the presence of N,N'-dimethyltryptamine leads to a 1-cyano-4-aminobutadiene whose formation is best explained by assuming formation of the intermediate aldehyde (Scheme 28)[108].



SCHEME 28

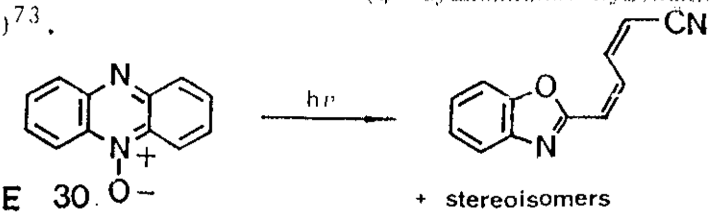
- U.V. irradiation of pentachloropyridine-N-oxide leads to an open-chain isocyanate whose formation is best accounted for by assuming the intermediate occurence of a six-membered lactam as shown in Scheme 29[109].



SCHEME 29

3-7-8 From Phenazine-N-oxides

Irradiation of phenazine-N-oxide leads by an unknown mechanism to the various geometric isomers of 2-(4'-cyanobutadienyl)benzoxazole (Scheme 30)[73].



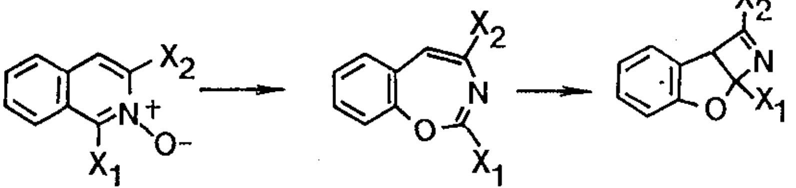
SCHEME 30

+ stereoisomers

3-8 Photoisomers of various structural types.

3-8-1 From isoquinoline-N-oxides.

1,3-Benzoaxepines, obtained by UV irradiation of isoquinoline-N-oxides, may undergo photoinduced electrocyclisation to the corresponding azacyclobutene isomers (Scheme 31)[52,106], a photoreaction type which is well known in the cycloheptatriene series[110]. These

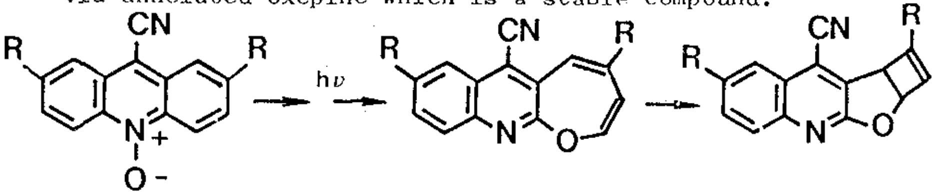


SCHEME 31

azacyclobutenes are easily hydrolysed, even by simple chromatography over silicic acid, and lead after elimination of ammonia to benzofurans[52].

3-8-2 From acridine-N-oxides.

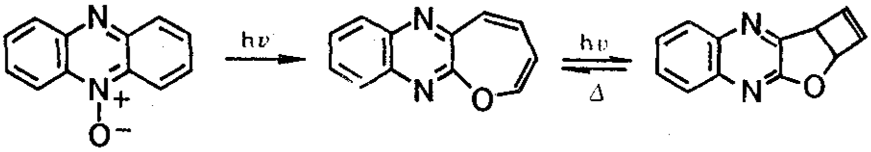
A similar photo-electrocyclisation has been described in the acridine-N-oxide series (Scheme 32) whereby a cyclobutene is obtained[75,80,98] via annelated oxepine which is a stable compound.



SCHEME 32

3-8-3 From Phenazine-N-oxides.

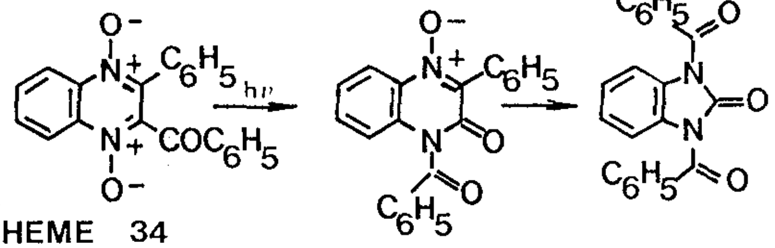
By analogy, phenazine-N-oxide leads to the isomeric oxepine and cyclobutene derivative (Scheme 33); this latter compound reverts back to the oxepine by thermal activation, a reaction pathway which cannot be a concerted one, according to the Woodward-Hoffmann rules[24,73].



SCHEME 33

3-8-4 From quinoxaline di-N-oxides

The photochemistry of aromatic bis-N-oxides has not received much attention yet. Still quinoxaline-bis-N-oxides lead to an interesting photoinduced ring contraction and give the corresponding benzimidazolones. For example 2-benzoyl-3-phenylquinoxaline-bis-N-oxide leads to the symmetrical 1,3-dibenzoylbenzimidazolone, probably via a lactam (Scheme 34)[111,112]

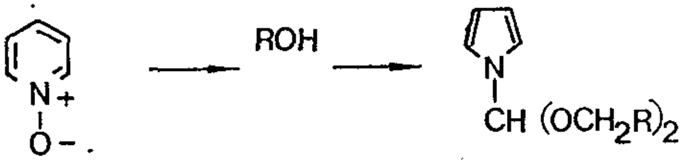


SCHEME 34

3-9 Photochemistry of aromatic-N-oxides in relation with the reaction medium.

3-9-1 Pyridine-N-oxides.

UV irradiation of pyridine-N-oxides in alcohols leads to N-formylpyrrole acetals (Scheme 35). Although no intermediates have been isolated, it is believed that solvolysis occurs at some intermediate step[101].

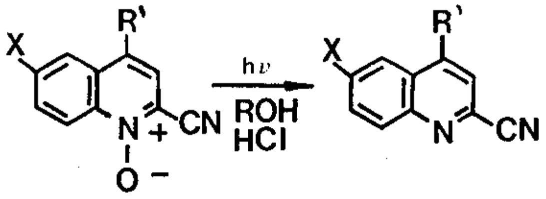


SCHEME 35

Cupric salts play an important role in the photochemistry of pyridine-N-oxides. Direct irradiation of pyridine-N-oxides by UV light in organic solvents or in water solution leads to various photoproducts, albeit in very low yields (vide supra). In the presence of copper sulfate or perchlorate and in water solution, most C_{2v} type pyridine-N-oxides lead to the corresponding photoproducts in preparative yields. For example pyridine-N-oxide leads to 2-formylpyrrole, in 2% yield in the absence, and in 40% yield in the presence of copper salts[113,114]. It is believed that a reversible REDOX mechanism is involved at the postulated nitrene intermediate stage which derives from the hypothetical 1,2-oxazepine[19,115].

3-9-2 Quinoline-N-oxides.

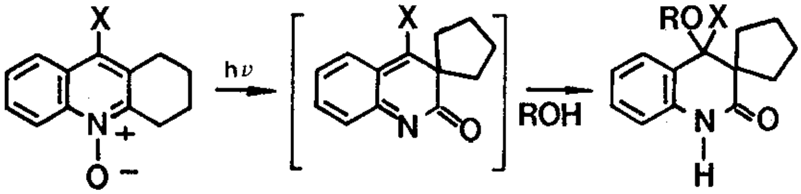
2-Cyanoquinoline-N-oxides, irradiated in various alcohols and in the presence of hydrochloric acid, lead to a mixture of 6-chloro-, 6-hydroxy- and 6-alkoxy 2-cyanoquinolines the distribution of which is a function of the nature of the alcohol and of the acid concentration (Scheme 36) . In concentrated sulfuric acid for example the 6-alkoxy derivative is the major product[116].



a) X = Cl
b) X = OH
c) X = OR

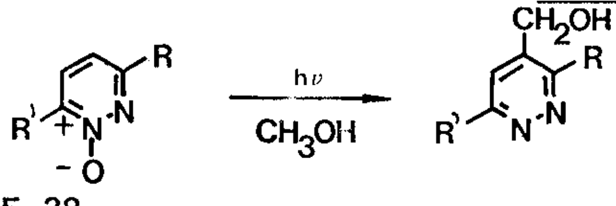
SCHEME 36

Alkoxy derivatives have also been described during UV irradiation of 2,3-tetramethylene quinoline-N-oxides, in methanol and ethanol whereby alcohol molecules add to C-4 in good to excellent yields,[66] probably after the rearrangement step to the spirolactams (Scheme 37).



SCHEME 37

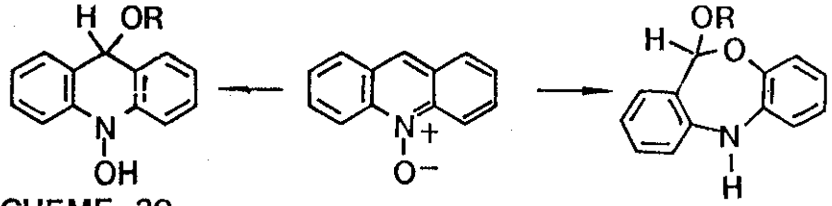
3-9-3 Pyridazine-N-oxides. Photoinduced 4-hydroxymethylation and concomitant oxygen abstraction have been observed with 3,6-disubstituted pyridazine-N-oxides in methanol solution, albeit in very low yield; a radical type mechanism has been proposed in order to account for this carbon-carbon bond formation (Scheme 38)[102].



SCHEME 38

3-9-4 Acridine-N-oxides. Two types of alkoxylations occur when acridine-N-oxides are irradiated in alcoholic solvents:

- alkoxylation at C-9 without rearrangement, a zwitterion being postulated as an intermediate (Scheme 39)[117];
- alkoxylation at C-9 with concomitant rearrangement to a dihydro dibenzo-1,4-oxazepine (Scheme 39)[90,98,118].



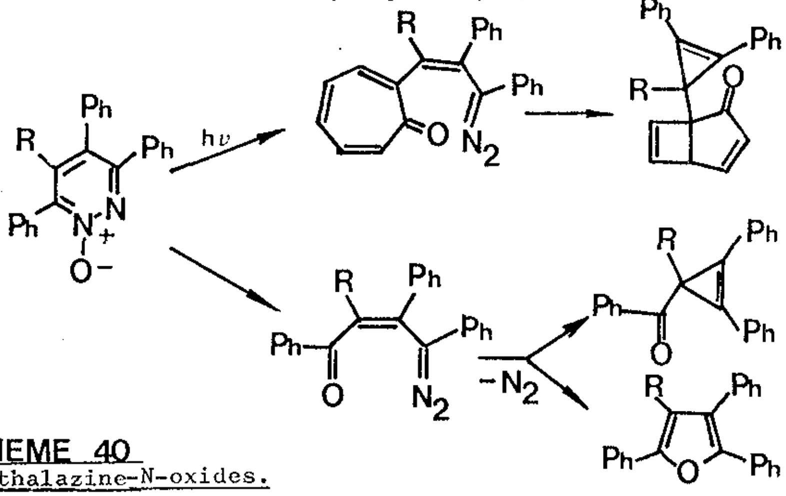
SCHEME 39

4 PHOTOCHEMISTRY OF SIX-MEMBERED CYCLIC AROMATIC AZINE-N-OXIDES

Pyridazine-, phthalazine-, cinnoline- and benzotriazine-N-oxides undergo peculiar photochemical reactions, usually with loss of a nitrogen molecule, leading thereby to " nonclassical photoproducts."

4-1 Pyridazine-N-oxides

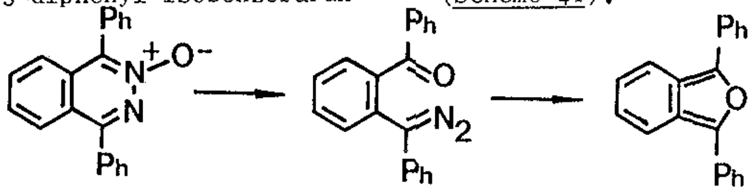
Although photoexcited pyridazine-N-oxides lead to atomic oxygen transfer on a preparative scale, they also undergo interesting ring contractions to cyclopropenylketones and furans via diazoketones which loose a nitrogen molecule. (Scheme 40)[119,120,121]. The diazoketones, which are rather unstable and coloured species, could nevertheless be characterised, especialy by IR spectroscopy[16].



SCHEME 40

4-2 Phthalazine-N-oxides.

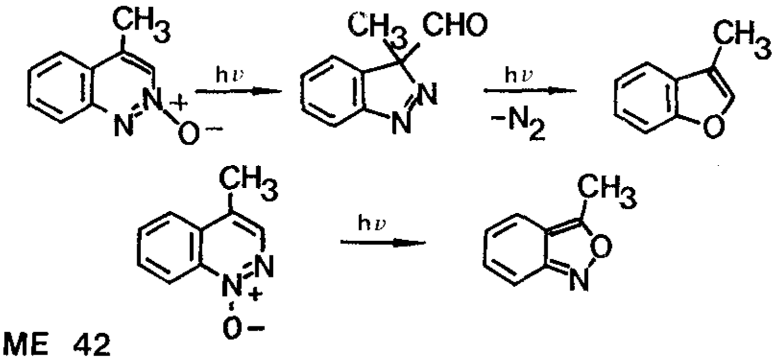
Phthalazine-N-oxides lead similarly to nonclassical photoproducts. For example 1,4-diphenyl-phthalazine N-oxide leads via a diazoketone to 1,3-diphenyl isobenzofuran[12,16] (Scheme 41).



SCHEME 41

4-3 Cinnoline-N-oxides

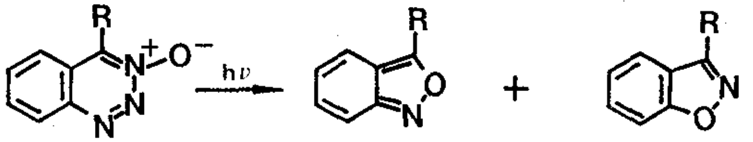
Photoexcited 4-methyl-2-oxocinnoline leads to 3-methyl-benzofuran which is supposed to occur via a 3-formyl-(3H)-indazole whereas 4-methyl-1-oxocinnoline leads to 3-methylanthranil (Scheme 42)[105].



SCHEME 42

4-4 Benzotriazine-N-oxides

Photoexcited 3-oxobenzotriazines loose a nitrogen molecule and lead to anthranils and to benzisoxazoles (Scheme 43)[122]



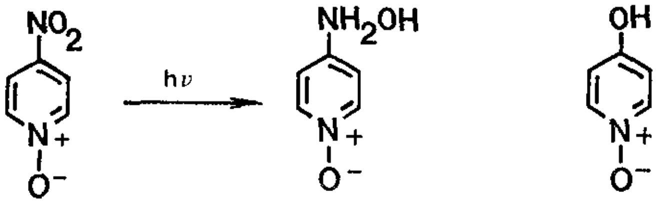
SCHEME 43

5 PHOTOINDUCED REACTIONS OF AROMATIC-N-OXIDE SIDE CHAINS

In some peculiar instances the photochemistry of aromatic N-oxides leads only to chemical modification on side chains to N-O bond cleavage.

5-1 With Nitro-Substituents

4-Nitropyridine-N-oxides undergo photoreduction of the nitro group leading in alcoholic solution either to the corresponding hydroxylamines or to the hydroxycompounds[51,123,124]. In aqueous alcoholic solutions quantum yield and flash-photolysis measurements suggest that the photoreduction initiates from an excited triplet state of the N-oxide which picks up a hydrogen atom from the alcohol[125,126,127](Scheme 44).



SCHEME 44

5-2 With Nitroso-Substituents.

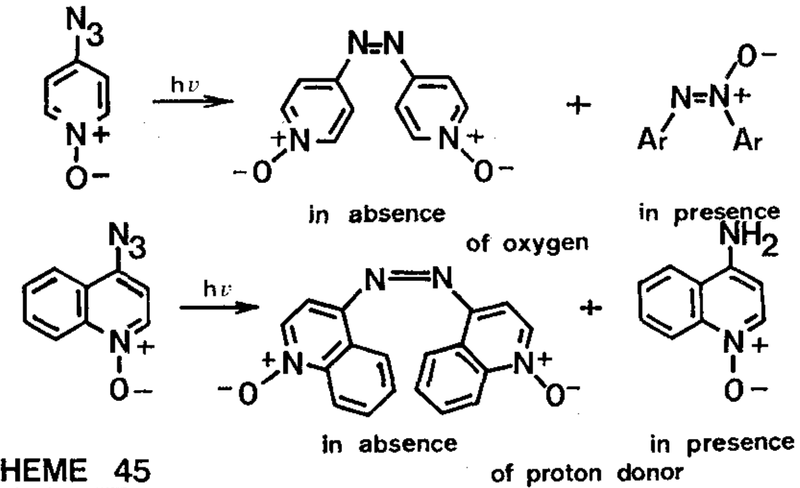
4-Nitrosopyridine-N-oxide is reduced photochemically in alcoholic solution, in the presence and in the absence of oxygen, to yield the hydroxylamine derivative[124].

5-3 With Hydroxylamine substituents

4-Hydroxylaminopyridine-N-oxide is photooxidized to the corresponding 4-nitropyridine-N-oxide[124].

5-4 With Azido substituents.

UV irradiation of azidopyridine- and 4-azidoquinoline-N-oxides leads to molecular nitrogen abstraction and concomitant formation of the corresponding unstable nitrene derivatives which may dimerise, lead to azoxy compounds or to amino-derivatives, depending upon the reaction conditions which are used (Scheme 45)[128,129]



SCHEME 45

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