

## RADICAL MECHANISM IN THE PHOTOREACTION OF ORGANIC *N*-OXIDES: OXYGEN TRANSFER FROM PHOTOEXCITED PARADIAZINE DI-*N*-OXIDES TO AMINES

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### Summary

Photolysis of paradiazine di-*N*-oxides in solution leads to the production of *N*-hydroxy-*N*'-oxyl radicals via hydrogen abstraction. For example, a chloroform solution of 2-methyl-3-acetylquinoxaline 1,4-dioxide gives the radical 1-hydroxy-2-methyl-3-acetylquinoxaliny-4-oxyl. In the presence of amines, photoinduced oxygen transfer has been observed and electron spin resonance studies have indicated that reaction leads to the formation of amine-derived nitroxide radicals in systems involving triethylamine and secondary amines. Thus, the two typical cyclic nitroxides pyrrolidinyl-1-oxyl and 4-hydroxy-2,2,6,6-tetramethylpiperidiny-1-oxyl are generated through photolysis of chloroform solutions containing 2-methyl-3-acetylquinoxaline 1,4-dioxide and the corresponding amines. The evidence presented suggests that the active oxygenating species are the lowest triplet states of the *N*-oxides generated by photolysis. Exciplexes formed through collision of the T<sub>1</sub> state *N*-oxides with the amines may be intermediates in the oxygen-transfer processes. Amine-derived radicals are generated from the exciplexes through further O-N bond formation and  $\alpha$  cleavage of the amine moiety.

### 1. Introduction

One of the reasons for the recent interest in the photochemistry of *N*-oxide compounds in solution is the application of the *N*-oxide photoreaction as a satisfactory enzyme-mimicking model for biochemical oxygen transfer, such as that brought about by the mono-oxygenase enzymes [1 - 6]. Various mechanisms for oxygen transfer involving *N*-oxides have been delineated, mainly based on the experimental evidence from conventional photolysis and product analysis [2 - 5]. More generally, our understanding of the mechanism for *N*-oxide photoreactions is less advanced, although *N*-oxide

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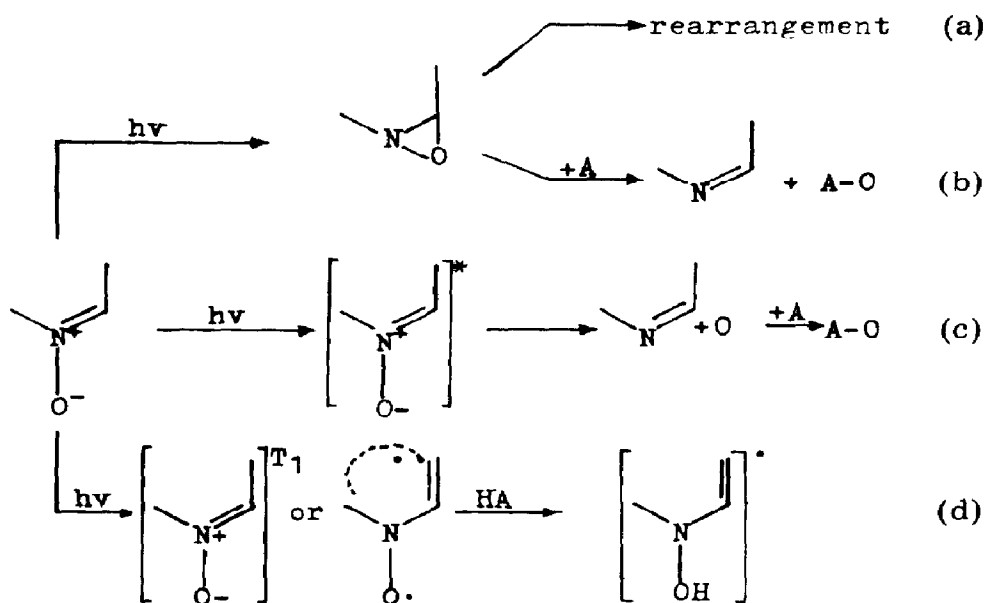
photochemistry has been the subject of frequent study [1, 7, 8]. Detailed mechanistic elucidation of these photoprocesses virtually requires additional sophisticated instrumental tools to search for the intermediates involved. Thus, in view of the established technique of electron spin resonance (ESR) [9] and related facilities of chemically induced dynamic electron polarization (CIDEP) and chemically induced dynamic nuclear polarization (CIDNP) observation [10] employed in photochemical research by many laboratories, the lack of such investigations on the possible radical mechanisms of the cycloaromatic amine *N*-oxide photoreactions is quite surprising.

Photoreactions of the *N*-oxides are classified into two groups: rearrangement and redox reaction (see Scheme 1). The former reaction, photoisomerization, is usually assumed to proceed via route (a). Evidence for a radical mechanism in *N*-oxide isomerization has been provided, for example, by observation of the external magnetic effect [11]. Similar profound magnetic effects have been found in the photochemistry of ketones [12]. The photoredox reaction almost exclusively consists of deoxygenation.

The deoxygenation, or in certain cases the oxygen transfer, is assumed by some researchers to proceed by route (b) [5, 13]. The hypothesis that oxygen is liberated directly from excited *N*-oxides and then intercepted by the acceptor A was developed by Ogawa *et al.* [3] and was supported by Rowley and Steedman [2] (shown by route (c)).

Many workers have suggested that the excited state involved in the photodeoxygenation reactions is the lowest triplet state [1].

A previous report [14] on some paradiazine di-*N*-oxides, however, suggested that the photoreduction process can be accomplished by hydrogen abstraction from the solvent (route (d)). Route (d) [14] is quite similar



Scheme 1.

to the photochemical behaviour of ketones that abstract hydrogen from solvents with the formation of neutral radicals such as aroxyl radicals [15, 16]. It seems obvious that there are some similarities between the photochemical properties of *N*-oxides and ketones.

Ketones are the most thoroughly and still the most frequently studied class of compounds in the field of organic photochemistry. As various paramagnetic species have been detected from ketone-containing photoredox systems (some recent examples can be found in refs. 17 - 21), the application of magnetic resonance techniques can be expected to shed light on the mechanism of *N*-oxide photoreactions.

Therefore, ESR studies have been extended to the systems involving both *N*-oxides and amines. The experimental findings, some preliminary accounts of which have already been reported [22, 23], do not indicate hydrogen abstraction (route (d)) as for photoexcited ketones, but provide evidence for oxygen transfer from the *N*-oxides to the amines producing amine-derived nitroxides. In this paper the experimental results for systems involving 2-methyl-3-acetylquinoxaline 1,4-dioxide (MAQO) and cyclic amines are given and the probable mechanisms are discussed.

## 2. Experimental details

The solvent chloroform was analytical grade and was further purified by treating overnight with  $\text{CaCl}_2$  followed by distillation in the presence of  $\text{P}_2\text{O}_5$ . Pyrrolidine was RP grade (Carlo Erba product) and further purified through distillation. High quality 2,2,6,6-tetramethyl-4-piperidinol was a gift from Dr. Zhang Fa from the Chemistry Department of Lanzhou University, China. MAQO was synthesized and purified by an improved method [24].

The variation in the UV absorption spectrum was measured at room temperature with a Shimadzu-365 UV-visible spectrophotometer. The solution was held in a quartz cell 1 cm thick and was bubbled with argon for 10 min. Then it was exposed to continuous illumination from the unfiltered light source of a 125 W high pressure mercury lamp placed at a distance of 20 cm.

For ESR measurements, a solution of MAQO and amine in chloroform in a quartz tube of outside diameter 4 mm was first bubbled for 30 min with oxygen-free argon and then photolysed *in situ* with unfiltered UV light from a 150 W xenon lamp. The distance between the lamp and the window of the resonance chamber was 50 cm. ESR spectra were recorded at the ambient temperature (about 20 °C) on a Varian E-115 ESR spectrometer. The spectrum was simulated by a Varian E-936 computer.

## 3. Results

Both the removal of dissolved oxygen in the solution and UV irradiation are necessary conditions for the successful observation of ESR spectra. Otherwise there will be no ESR signals observable from the systems.

Thus the radical pyrrolidinyl-1-oxyl (2) is produced only during the photolysis of the oxygen-free solution containing MAQO and pyrrolidine (1) in chloroform:

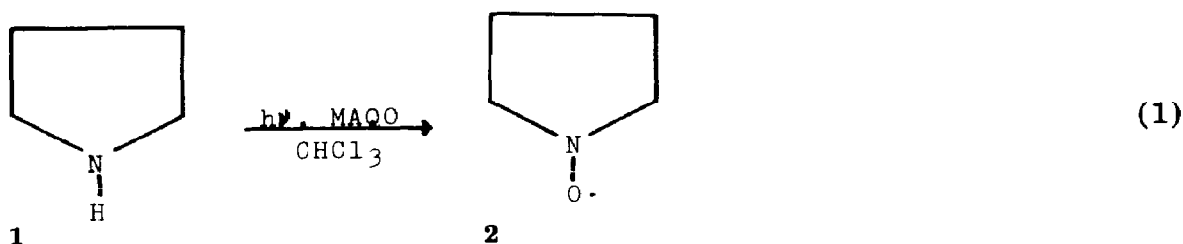


Figure 1 shows the ESR spectrum of 2 with  $g = 2.0059$ . The experimental spectrum and the simulated spectrum are in good agreement, indicating a triplet from the nitrogen atom with  $a(\text{N}) = 14.85$  G and a quintet from the four  $\beta$ -hydrogens with  $a(\text{H}) = 19.41$  G. The spectrum immediately disappears on breaking off UV irradiation and its intensity is recovered upon

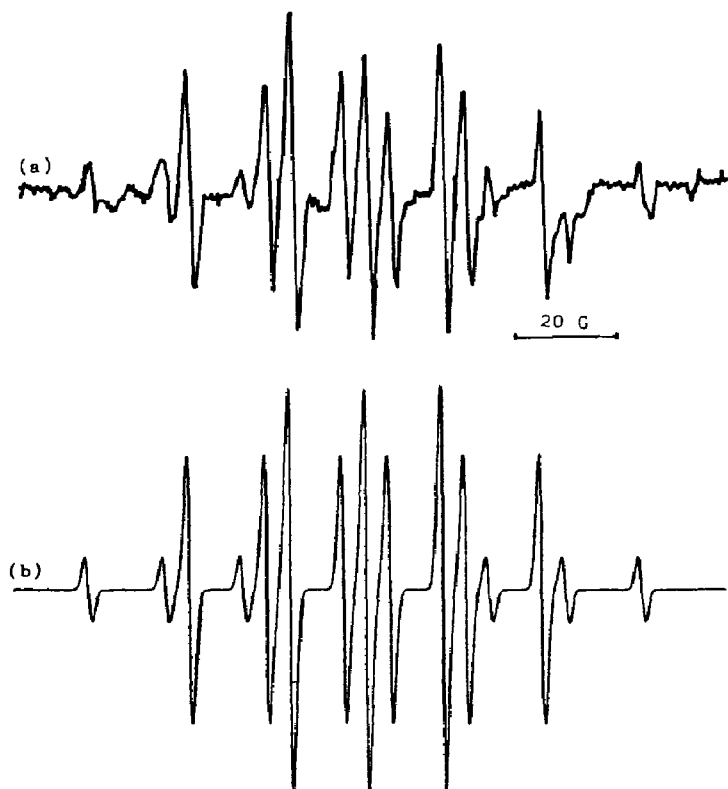
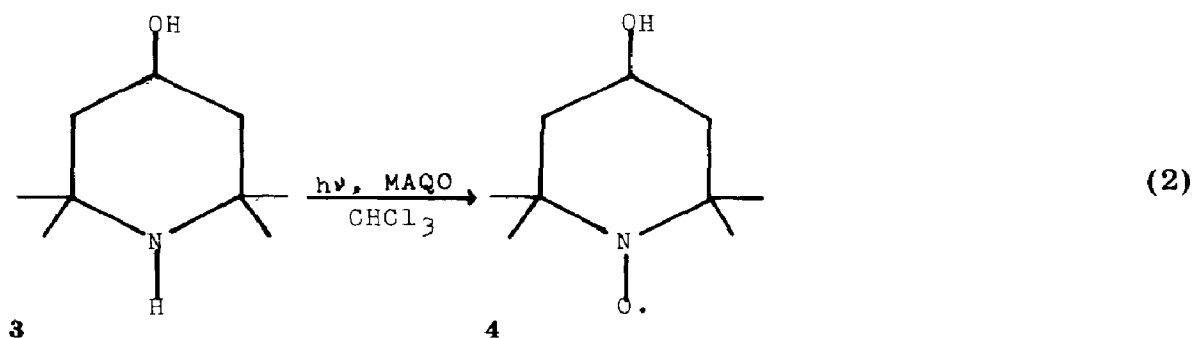


Fig. 1. (a) Experimental ESR spectrum of 2 from a system of 1 (4 vol.%) and MAQO (0.5 M) in chloroform during photolysis, with scan range 400 G, microwave power 10 mW, modulation amplitude 1.0 G and scan time 8 min; (b) simulated spectrum with gaussian line shape.

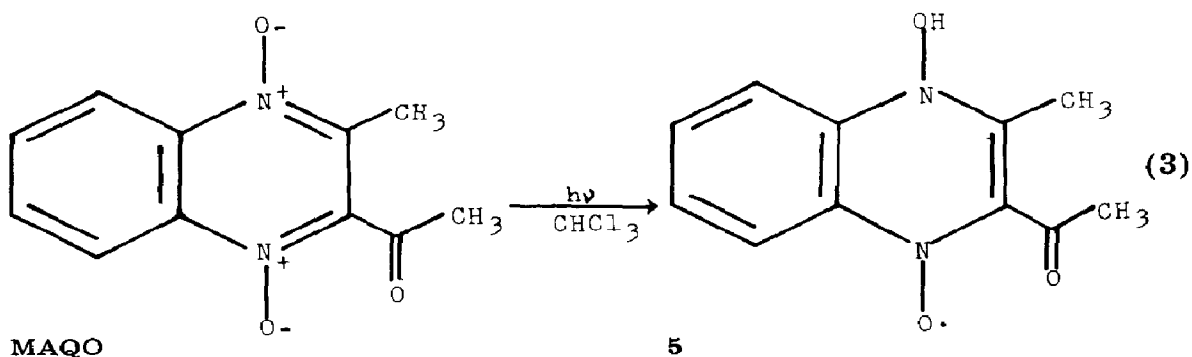
subsequent irradiation, and the same spectrum can be recorded repeatedly in this way. This shows that there is a definite steady state radical concentration for this system during photolysis.

For 2,2,6,6-tetramethyl-4-piperidinol (3) there is also no detectable ESR spectrum before exposure to UV irradiation. However, triplet line signals appeared and increased steadily during irradiation. It is interesting that the spectrum continues to increase until a certain intensity is reached within about 2 min. The radical thus produced is quite persistent. Over a period of about 2 h, there was no apparent diminution of the spectrum. This spectrum (see Fig. 2) is confidently assigned as the radical 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxyl (4) generated through photo-oxidation by MAQO and accumulated in the solution:



The four methyl groups in the  $\beta$  positions stabilize the radical. It is because of this stability that piperidinyl-1-oxyl radicals with basic structures similar to 4 are the most extensively studied nitroxide spin labels [25]. The spectral data measured from Fig. 2. for radical 4 are  $g = 2.0061$  and  $a(N) = 15.84$  G.

The photochemical activity of heteroaromatic *N*-oxides is notable. As shown in Fig. 3, a solution of MAQO in chloroform undergoes photofading under the influence of UV irradiation. The same is true for unsubstituted quinoxaline 1,4-dioxide [26]. Our previous investigations [14] showed that the photolysis of MAQO in neat chloroform leads to the formation of the nitroxide 1-hydroxy-2-methyl-3-acetylquinoxaliny-4-oxyl (5) from MAQO itself:



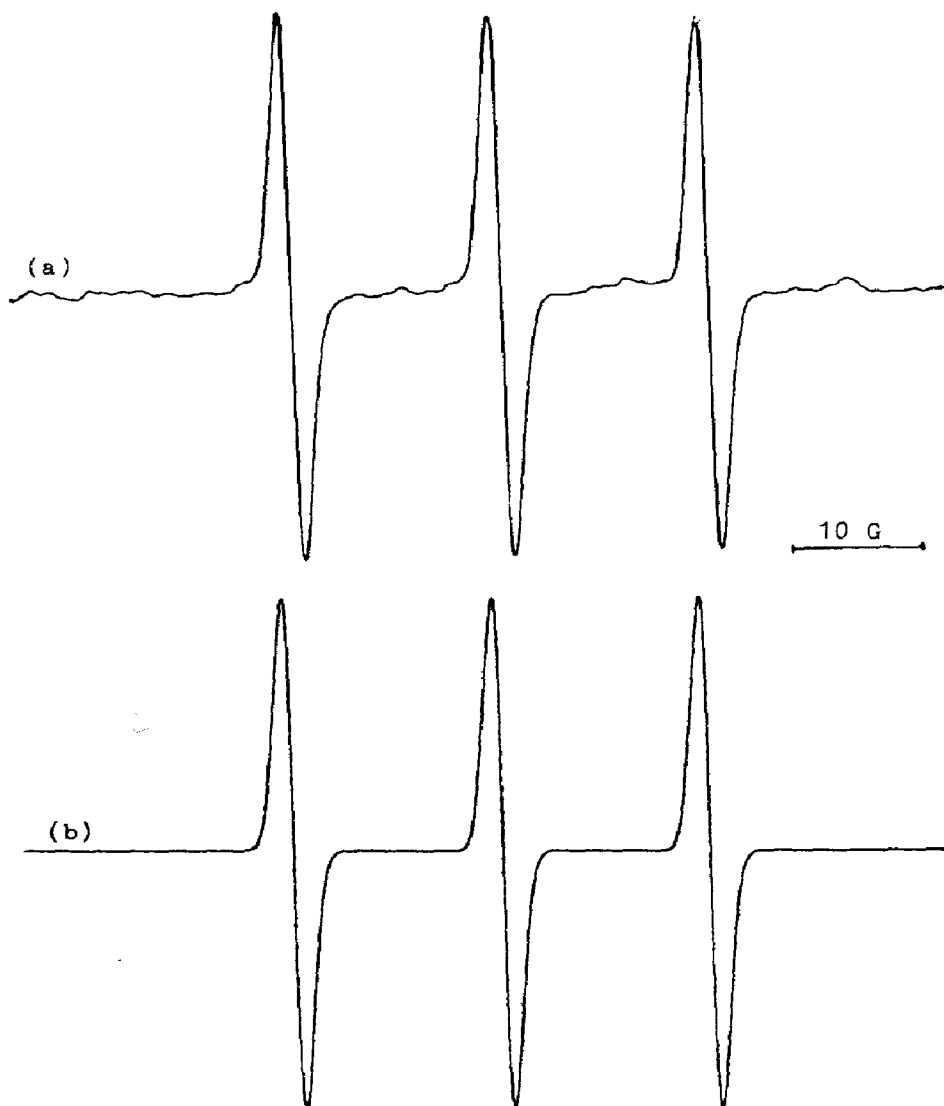
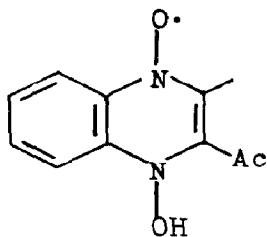


Fig. 2. (a) Experimental ESR spectrum of 4 from a system of 3 (0.5 M) and MAQO (0.5 M) in chloroform recorded 5 min after a 10 s UV irradiation; (b) simulated spectrum with scan range 200 G, gaussian line shape and linewidth 1.03 G.

Figure 4 shows the ESR spectrum of 5 and its simulated spectrum. The alternative form of 5 is 6.



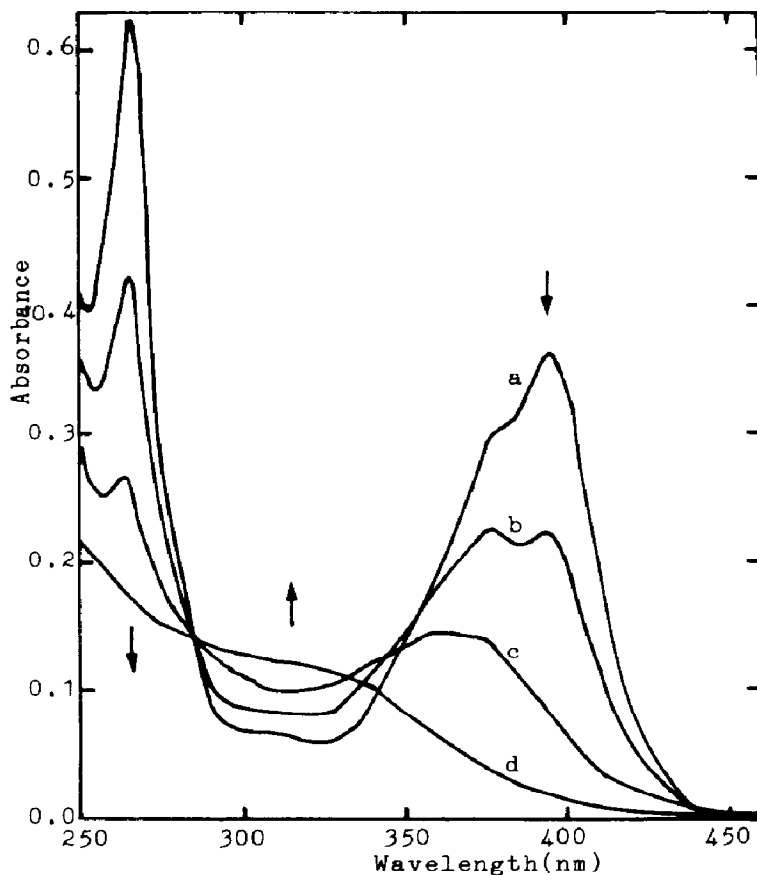


Fig. 3. Changes in the electronic spectrum of MAQO in chloroform on UV irradiation for various times: curve a, 0 s; curve b, 40 s; curve c, 100 s; curve d, 250 s. The initial concentration of MAQO was  $3.2 \times 10^{-5}$  M.

Intermediate neglect of differential overlap (INDO) molecular calculations show that 5 is more stable than 6, so 5 is assumed to be a more reasonable structure.

#### 4. Discussion

When primary amines, such as *tert*-butylamine, cyclohexylamine and *n*-butylamine, are included in photolytic systems containing *N*-oxides, the ESR signals of *N*-oxide-derived nitroxides which should be formed through processes such as reaction (3) cannot be detected in ESR experiments. Usually, no well-defined ESR spectra can be recorded in these cases. As these reactions may be quite distinct, the following discussion will be confined only to systems containing other kinds of amines.

As electron-rich Lewis bases, amines are good electron donors and easily form charge transfer exciplexes with electron acceptors such as ketones during photolysis in electron transfer processes. In contrast, amines are hydrogen donors in some redox reactions. Moreover, amines can also

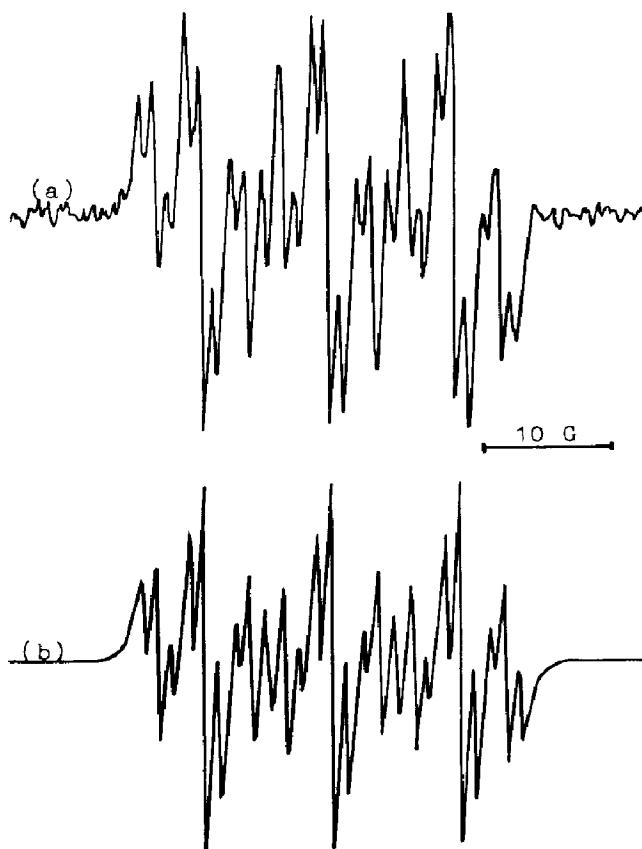


Fig. 4. (a) Experimental ESR spectrum of 5 from a system of MAQO in neat chloroform, recorded during photolysis; (b) simulated spectrum with scan range 200 G, Lorentzian line shape and linewidth 0.60 G. The spectral data have been reported previously [14].

be good oxygen acceptors and this is another characteristic of amines as reductants.

Triethylamine and dialkylamines were oxidized in the photoreaction systems containing heteroaromatic *N*-oxides. Amine-derived nitroxides were detected in these systems by ESR analysis. Since the oxygen dissolved in the solutions was removed in the experiments, the oxygen in the nitroxides (see Tables 1 and 2) must be derived from the aromatic *N*-oxides. It is conceivable that the initial intermolecular step for the nitroxide formation process is the oxygen transfer between the photoexcited *N*-oxides and the amines. It is worth stressing a very interesting point that oxygen has been transferred from one kind of amine (an amine from an amine *N*-oxide) to another kind of amine (such as a free amine involved in the system), while under the usual conditions heteroaromatic *N*-oxides do not seem to be reactive in amine media and many heteroaromatic *N*-oxides have been synthesized and isolated from the reaction solvent amines [27]. Thus the primary process involved in the present instances (such as reactions (1) and (2)) might be oxygen transfer from the cycloaromatic amine oxide to the aliphatic amine.



TABLE 1

Observed hyperfine coupling constants (in gauss) and  $g$  values for diethyl nitroxide formed through photolysis of solutions containing triethylamine and various  $N$ -oxides [22]

Reaction mixture	Hyperfine coupling constants		$g$ values
	$a(N)$	$a(\beta-H)$	
8-C <sub>6</sub> H <sub>6</sub>	14.87	10.26	2.0061
9-CHCl <sub>3</sub>	15.36	10.51	2.0059
9-C <sub>6</sub> H <sub>6</sub>	14.89	10.27	2.0060
10-C <sub>6</sub> H <sub>6</sub>	14.82	10.36	2.0061
MAQO	14.79	10.09	2.0060
Benzofuroxan	14.87	10.16	2.0060

TABLE 2

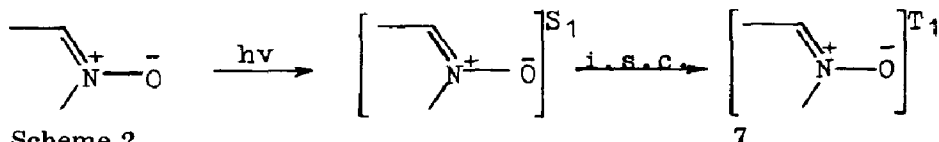
Observed hyperfine coupling constants (in gauss) and  $g$  values for nitroxides formed through photolysis of solutions containing MAQO and various dialkylamines in chloroform [23]

Radical	Amines	$a(N)$	$a(\beta-H)$	$g$ values
Di- <i>n</i> -propyl nitroxide	Di- <i>n</i> -propylamine (3.0 vol.%)	15.03	10.25	2.0059
Diisobutyl nitroxide	Diisobutylamine (3.0 vol.%)	14.73	9.61	2.0058
Diallyl nitroxide	Diallylamine (5.0 vol.%)	15.45	9.41	2.0059
Dicyclohexyl nitroxide	Dicyclohexylamine (10 vol.%)	14.99	4.35	2.0059

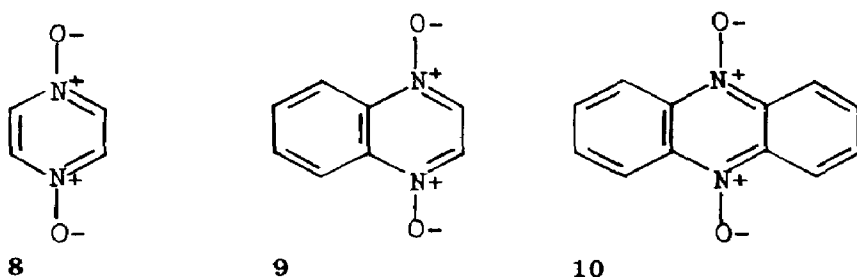
Incidentally, the possibility of aromatic- $N$ -oxide-sensitized photo-oxidation of the amines to produce nitroxides, as has been reported with certain ketones as photosensitizers [28], should obviously be ruled out. This is simply from the experimental fact that all the reaction mixtures described in Tables 1 and 2, if air saturated, will not show any ESR spectra at room temperature, even if the systems are treated by prolonged continuous UV illumination. Photolytic systems of  $N$ -oxides in amine-free solvents, *e.g.* MAQO in chloroform (reaction (3)), also fail to give nitroxides if the solutions are air saturated [14].

Many researchers have omitted to consider the characteristics of the excited states of the  $N$ -oxides involved in the photodeoxygenation processes [2 - 6], but Pietra *et al.* [29] have announced that the photochemical reactions between 2-nitrophenazine  $N$ -oxide with amines take place partly from the excited singlet state of the  $N$ -oxide. Nevertheless, since it is common knowledge that ground state dioxygen is an efficient quencher of the lowest triplet states of many organic molecules in solution, the photoexcited

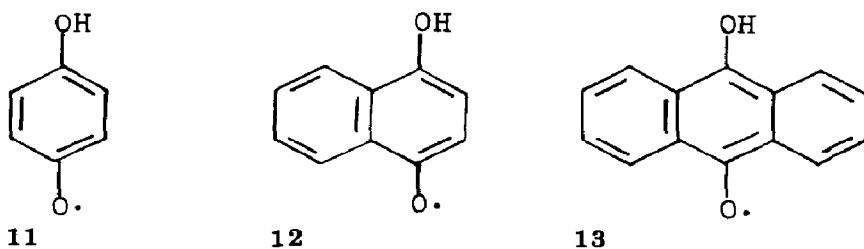
*N*-oxides in the present cases are therefore most likely to be in their lowest triplet states (7) (Scheme 2) when they are attacked by the substrate amines to start the oxygen transfer. This is supported by the present experimental evidence which shows that dissolved oxygen quenches the oxygen-transfer processes and consequently hinders amine-derived nitroxide formation. Photoredox reactions between *N*-oxides and chloroform (see reaction (3) as an example) are also believed to be initiated from T<sub>1</sub> states (7).



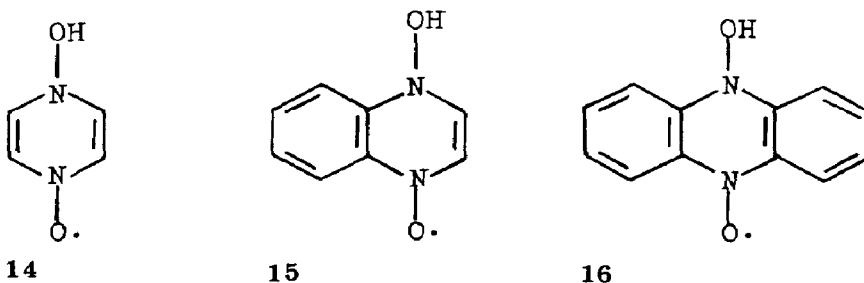
The photoreactions of pyrazine 1,4-dioxide (8) [30], quinoxaline 1,4-dioxide (9) [26] and phenazine 9,10-dioxide (10) [31]



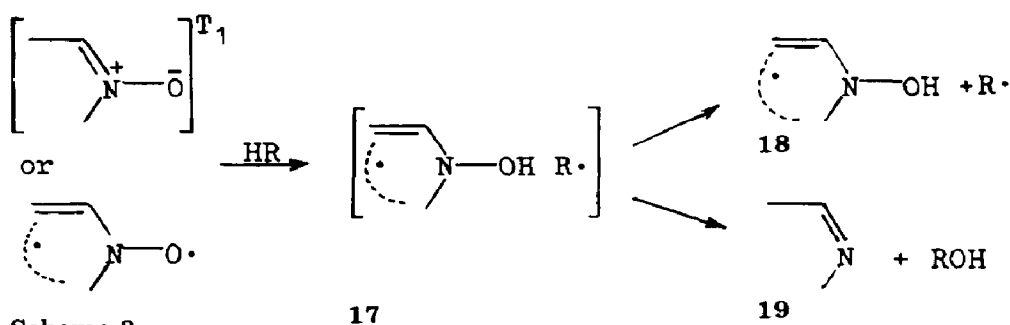
have been reported separately in this journal. As has been stated previously, the photoinduced hydrogen abstraction reactions of ketones lead to the production of radicals, such as neutral radicals 11, 12 and 13



from paraquinones [15]. Analogously, oxyl radicals 14, 15 and 16

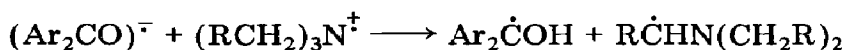
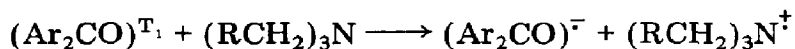


have been produced from paradiazine di-*N*-oxides 8, 9 and 10 [14]. Recently, the author has observed weak yet identifiable well-resolved ESR spectra, which should be assigned to 14 ( $g = 2.006$ ,  $a(N) = 13.5$  G), from the photolytic system of 8 (saturated) in 1,4-dioxane. A detailed description of the novel radicals 14, 15 and 16 will be published elsewhere. One significant aspect of the detection of the radicals 14, 15 and 16 as well as 5 is its strong support for the radical mechanism for the oxygen-transfer processes involved in hydroxylation of hydrocarbon compounds (Scheme 3). This is in concurrence with the radical mechanism suggested for the corresponding biological processes [6]. The free radical 18, which is derived from radical pair 17 and escapes from the solvent cage, is persistent enough to be detected by the ESR technique. The decay of 18 can also result in 19 as has been suggested previously [14]. The precursor of 17 is the triplet state generated via the conventional pathway shown in Scheme 2, or diradicals [14].



Scheme 3.

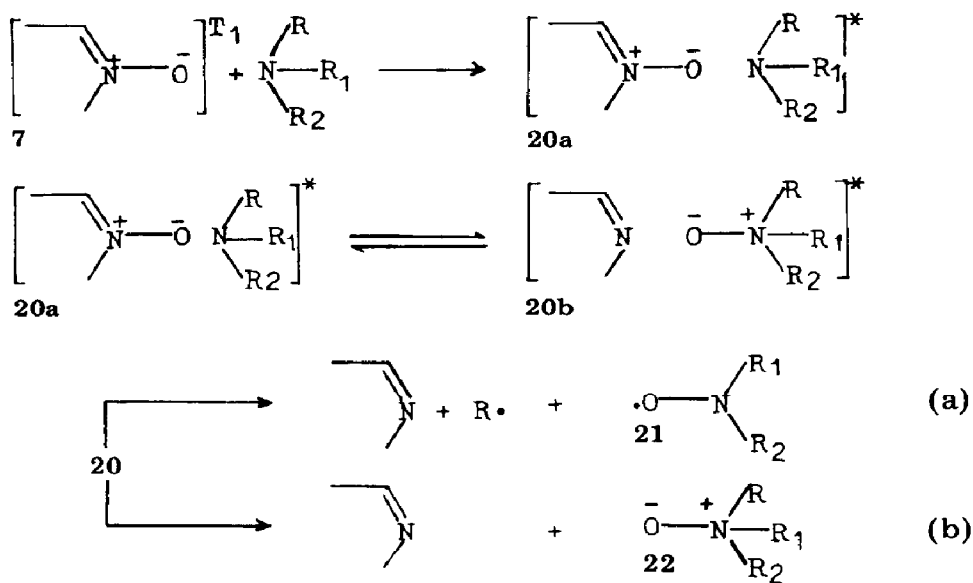
However, in many photochemical reactions of ketones with amines [21, 32] (see Scheme 4), radical anions are formed in the initial step. Thus, if *N*-oxides such as 8, 9, 10 and MAQO react with triethylamine, a good electron donor, persistent radical anions [33] should be produced. But, as stated above, only diethyl nitroxide was detected (Table 1); an extension of these studies to the systems involving dialkylamines also provides similar results (see Table 2).



Scheme 4.

It is worth pointing out that the five- and six-membered cyclic nitroxides have structures typical of nitroxide spin labels and play an especially important role in the studies of chemical and biological systems by the ESR spectroscopic technique [25]. Therefore, the experimental results represented by reactions (1) and (2) also provide additional evidence that photo-excited *N*-oxides can be used as oxidizing agents in the preparation of nitroxides from the corresponding amines.

The suggested reaction mechanism shown in Scheme 5 is based on the present ESR observations and the results summarized in Tables 1 and 2. The



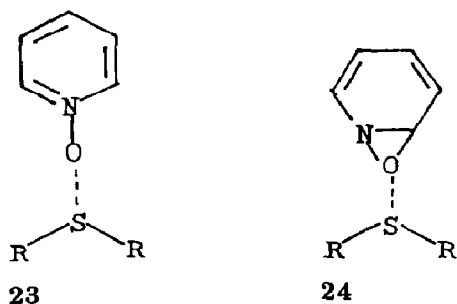
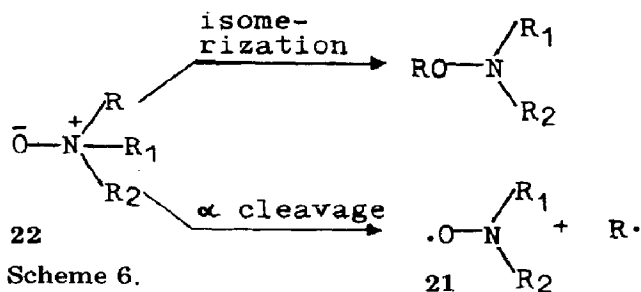
Scheme 5.

exciplex **20** is formed through collision of the lowest triplet states of the *N*-oxides with the amines.

Electron redistribution within the exciplex **20** leads to the formation of a new bond bridged by an oxygen atom. In all the known oxygen-transfer reactions, such as sulfoxidation, aromatic and aliphatic hydroxylation and epoxidation, the active oxygenating species generated on photolysis of *N*-oxides has been commonly observed to exhibit electrophilic behaviour [2 - 5]. In spite of the oxygen atom within the dipolar  $\overset{+}{\text{N}}-\overset{-}{\text{O}}$  function being electron rich in the ground state [34], a photoinduced  $n-\pi^*$  transition might endow the oxygen centre with certain electrophilic characteristics in the  $T_1$  state. In such a case, the oxygen centre in the *N*-oxide will approach the nitrogen centre of the amine to form the transition state exciplex **20**.

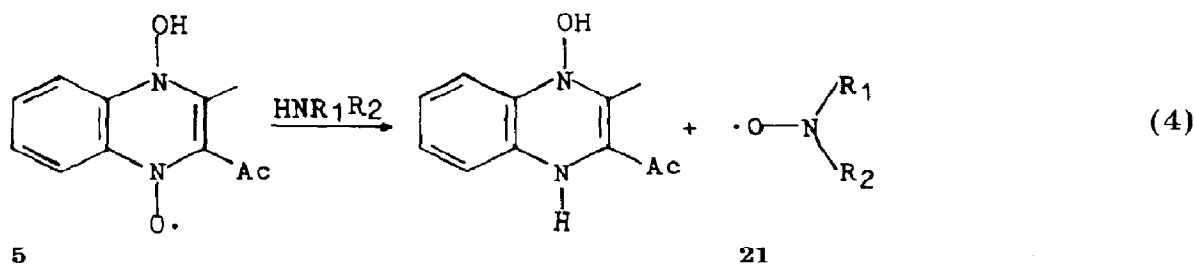
The dialkyl nitroxides **21**, including **2** and **4**, are assumed to be produced via route (a) from exciplex **20**, probably from **20b** where the O—NRR<sub>1</sub>R<sub>2</sub> bonding is stronger than another partial bonding. The  $\alpha$  cleavage within the amine moiety occurs in route (a). The leaving group R is exclusively a hydrogen atom when the substrates are secondary amines. Whether or not **22** is produced as a final product (route (b) in Scheme 5) cannot be concluded before product analysis is performed, but this is quite possible according to the fact that triphenylphosphine can accept oxygen from photoexcited *N*-oxides to generate a *P*-oxide which is similar to **22** [13]. If **22** is produced, then isomerization and cleavage may be possible (Scheme 6), the isomerization being most probable for the cases with secondary amines as substrates where R is H.

Other possible transition states have been proposed. Transient species **23** and **24**



have been considered for photochemical sulphur oxidation [5], where 23 resembles 20 in Scheme 5. However, the authors of ref. 5 prefer 24. The precursor of 24 is oxaziridine derived from *N*-oxides (route (b) in Scheme 1). Rowley *et al.* [2] deduced more recently that the oxygenating species is most probably not oxaziridine in the similar photoreactions of *N*-oxides and triarylphosphine sulphides. Moreover, the reactions of phenyl compounds with photoexcited *N*-oxides [3, 4] and with  $\text{O}(^3\text{P})$  or oxene [35] are different in product distribution, which may be an indication that the oxene [3, 4] is not involved in these oxygen-transfer processes.

The secondary-amine-derived nitroxides might also be produced in the manner shown in reaction (4) with MAQO as a representative *N*-oxide:



The oxygen transfer takes place between nitroxide 5 and the secondary amines, and 5 is then assumed to be the oxidizing species. We consider this to be unlikely for the following reasons. First, the nitroxide, as a conjugated oxyl radical, is quite stable and unreactive, although other kinds of oxyl radicals such as  $\text{R}-\text{OO}\cdot$  might be suitable oxidants [36]. Second, this is practically an intermolecular exchange of an oxygen atom for a hydrogen atom at two nitrogen centres. There cannot be any remarkable bond energy gain for this proposed double replacement thermochemical process. Further-

more, the known reduction reactions of nitroxides are usually accomplished by hydrogen abstraction [37, 38]. To exclude this possibility confidently by experiment, we dropped some dicyclohexylamine into a sample tube containing the chloroform solution of MAQO described previously in which radical 5 had been detected by ESR, shook it for a while and inserted it into the resonance chamber. No ESR spectrum of dicyclohexyl nitroxide developed from the mixture, but the signals of 5 had disappeared. This may be due to the decay of 5 being accelerated by certain unknown interactions between 5 and the amine. This experiment provides sufficient evidence to rule out the possibility of reaction (4), yet this simple experiment should be repeated more carefully.

## 5. Conclusions

Photoreactions in systems of the heteroaromatic *N*-oxides and triethylamine or secondary amines yield the amine-derived nitroxides. The process for the production of the *N*-oxide-derived nitroxides is efficiently depressed by the presence of various aliphatic amines. The photoreactions in all these cases are suggested to initiate from the lowest triplet state of the *N*-oxides and proceed via exciplexes of the photoexcited *N*-oxides and the amines.

It is evident that the results of the present ESR studies of the radicals reflect some important features of the photoreactions between the cycloaromatic amine *N*-oxides and certain amines, although more detailed and quantitative studies are required to provide additional insight into the reaction mechanisms.

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