probably indicates that any exciplex formed decays with a lifetime of less than nanoseconds. Ottolenghi[12] has found that the spectra of arene–amine exciplexes normally contain bands similar to those found in the spectra of the related ion radicals. In particular, the exciplex from TMPD and biphenyl shows transitions like those of TMPD$^+$ and the biphenyl anion radical.[13] A similar pattern is found in the exciplex spectrum of anthracene-*N*,*N*-diethylaniline.[14] In each of these cases the absorptions are relatively strong. We presume that any analogous exciplex from TMPD and RUB should have been observable had it lived long enough. The fact that no exciplex emission is observed also limits that possible exciplex lifetime. The radiative lifetime of RUB fluorescence is $\sim$16 ns and the radiative lifetime of an exciplex should be of the same order of magnitude. We could have easily detected an emission quantum yield of 0.01; so the true lifetime of an exciplex would have to be less than a nanosecond to obliterate any detectable fluorescence. We conclude that either no exciplex is formed or that, if one is formed, it decays with a rate constant of 10^{10} s^{-1} or greater.

Acknowledgments. This work was supported by grants from the National Science Foundation (G.S.H.) and from the National Institutes of Health (D.S.K.).

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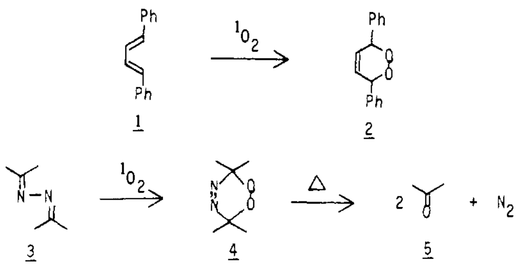
Received August 15, 1978

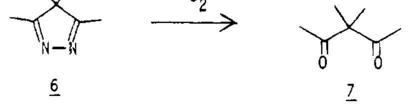
Photooxidation of Azines. Evidence for a Free-Radical Oxidation Initiated by Singlet Oxygen

Sir:

The reaction of singlet oxygen with conjugated dienes (reaction with *trans,trans*-1,4-diphenyl-1,3-butadiene[1] (**1**) is shown below) is well known.[2] The simplest view of this reaction as a concerted [2 + 4] cycloaddition is widely accepted.[2] The photooxidation of acetone azine (**3**) to tetramethyl-1,2-dioxa-4,5-diazine (**4**) has recently been reported,[3] and the similarity of the course of this oxidation with that of dienes prompted us to investigate the mechanism for the azine oxidation. We now report that the photooxidation of acetone azine proceeds via a free-radical pathway initiated by singlet oxygen.



Competitive photooxidation[4] of **3** vs. tetramethyl-4*H*-pyrazole (**6**) produces acetone (**5**) and diketone **7**, respectively, as the sole products by VPC analysis. The relative rate of oxidation (Table I) of **3** is three times that of **6**, and this rate ratio is moderately independent of solvent and sensitizer. Since **3** is significantly distorted from the cisoid conformation[5] and since **6** is restricted to the cisoid form, the relative rate of oxidation of **6** is predicted to be much larger than that of **3** assuming a concerted [2 + 4] cycloaddition. The observed rate ratio is inconsistent with this view.



The results of the competitive photooxidation of **3** with **1** are provided in Table II. Both compounds are similary reactive (k^{rel} of **1** to **3**, 4.5 in CDCl$_3$). This relative rate of oxidation of **3** to **1** is moderately independent of sensitizer (Table II), and both reactions are inhibited by singlet oxygen quenchers, Dabco and β-carotene (Table III). A remarkable difference in their reactivity, however, is that the oxidation of acetone azine is completely quenched while that of the diene is moderately unaffected by the addition of 2,6-di-*tert*-butyl-*p*-cresol, a free-radical scavenger (Table III). These results are con-

Table I. Relative Rates of Photooxidation of Acetone Azine (**3**) and Tetramethyl-4*H*-pyrazole (**6**)

solvent[a]	sensitizer[b]	k^{rel} (**3**:**6**)[c]
CCl$_4$	10^{-4} M TPP	3.2
CCl$_4$	10^{-6} M TPP	3.8
CH$_2$Cl$_2$	10^{-4} M TPP	3.3
CHCl$_3$	10^{-4} M TPP	3.0
CHCl$_3$	10^{-4} M MB	3.8
CDCl$_3$	10^{-4} M TPP	3.2
CFCl$_3$	10^{-4} M TPP	3.1

[a] $[\mathbf{3}]_0 = [\mathbf{6}]_0 = 0.2$ M; $T = -20$ °C. [b] TPP, tetraphenylporphyrin; MB, methylene blue. [c] Relative rates were determined by monitoring product formation by VPC: 1/4 in. × 10 ft 15% SE-30 on Chromosorb P at 50 °C.

Table II. Effect of Solvent and Sensitizer on the Relative Rates of Photooxidation of Acetone Azine (**3**) and *trans,trans*-1,4-Diphenyl-1,3-butadiene (**1**)

solvent	sensitizer[a]	k^{rel} (**1**:**3**)
CDCl$_3$[b]	TPP	4.5
CDCl$_3$[b]	MB	3.3
CDCl$_3$[b]	Ⓟ-RB	3.6
C$_6$F$_6$[c]	TPP	3.6
CCl$_4$[c]	TPP	3.5

[a] TPP (10^{-4} M), MB (10^{-5} M), Ⓟ-RB, polymer-anchored Rose Bengal[12] (100 mg/10 mL). [b] $[\mathbf{1}]_0 = [\mathbf{3}]_0 = 0.1$ M; $T = -20$ °C. [c] $[\mathbf{1}]_0 = [\mathbf{3}]_0 = 0.025$ M; $T = 0$ °C.

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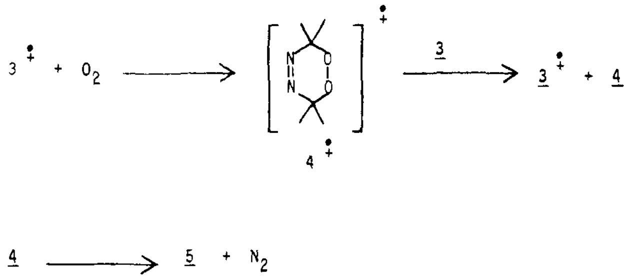
Table III. Effect of Additive on the Relative Rates of Photooxidation of Acetone Azine (**3**) and *trans,trans*-1,4-Diphenyl-1,3-butadiene (**1**)

additive[a]	k^{rel} (**1**:**3**)
none	4.5
5×10^{-4} M Dabco	no reaction after 7 h
5×10^{-4} M β-carotene	no reaction after 7 h
1.8×10^{-2} M 2,6-di-*tert*-butyl-*p*-cresol	>100
10^{-3} M $C(NO_2)_4$	4.2

[a] $[1]_0 = [3]_0 = 0.1$ M; $T = -20$ °C; sensitizer, 10^{-4} M TPP in $CDCl_3$.

Scheme I



sistent with a free-radical oxidation of **3** initiated by singlet oxygen. The similarity of relative rates of oxidation in solvents ($CDCl_3$, CCl_4) capable of halogen-chain reactions[6] and in those incapable of such reactions (e.g., C_6F_6) indicates the unimportance of halogen-atom initiation in this oxidation.

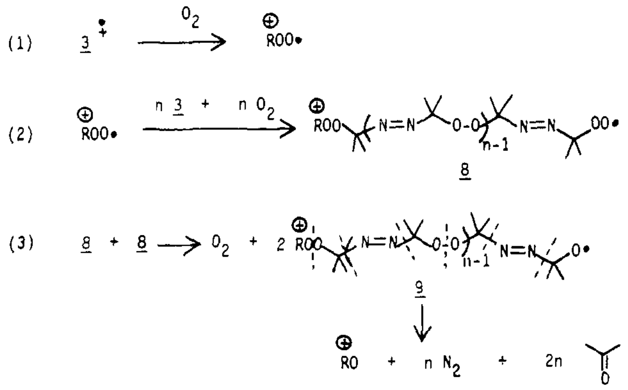
In view of recent reports[6] of free-radical initiated photooxidations not involving singlet oxygen, additional experiments probing the involvement of singlet oxygen in the azine oxidation were performed: (1) the oxidation of **3** is initiated[7] by triphenyl phosphite ozonide, a known source of singlet oxygen;[8] and (2) the triphenyl phosphite ozonide initiated oxidation of **3** is quenched by the addition of 10^{-3} M β-carotene. These results argue for singlet oxygen as the active oxidant.

One possible mechanism for the initiation of this oxidation involves electron transfer from **3** to singlet oxygen, generating superoxide ion and azine cation radical. Subsequent initiation by superoxide ion seems unlikely since independent attempts to oxidize **3** with potassium superoxide were unsuccessful and

$$\underline{3} + {}^1O_2 \longrightarrow \underline{3}^{\cdot+} + O_2^{\cdot-}$$

since the photooxidation of **3** was uninhibited by tetranitromethane (Table III), a superoxide scavenger.[9] Initiation and propagation by azine cation radical, however, may proceed by a mechanism (shown for **3** in Scheme I) analogous to that reported by Tang et al.[10] for the oxidation of the cation radical of ergosteryl acetate. Tetramethyl-1,2-dioxa-4,5-diazine (**4**), however, has never been observed in low temperature ^1H NMR spectra of photooxidized solutions of **3** with our conditions. As a result, we believe that an alternate mechanism for the propagation steps (not involving products like **4**) must be considered (Scheme II). Copolymerization of azine and oxygen as shown in (2) might produce a polymeric azo peroxy radical **8**. Dimerization of **8**, as with other peroxy radicals,[11] would produce alkoxy radical **9** that would be expected to undergo β scission as shown in (3) to produce the observed products.

Scheme II



Further characterization of the course of the photooxidation of azines is in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Office of Research and Projects of Southern Illinois University at Edwardsville for support of this work.

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Received March 29, 1979