Mechanistic Investigation of the Acenaphthenequinone Sensitized Bartlett Photoepoxidation of Olefins. Concomitant Oxidation of the Sensitizer

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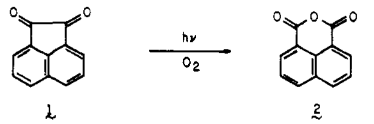
Received August 25, 1978

Photolysis of acenaphthenequinone in CH_2Cl_2 solution continuously saturated with oxygen generates 1,8-naphthalic anhydride in 80% isolated yield. When an olefin is included in the reaction solution it is converted to a mixture of oxidized products consisting mainly of allylic hydroperoxide and epoxide. It is demonstrated that the quantum efficiency for quinone oxidation is independent of quinone and olefin concentration. A mechanism is suggested for which an initial reaction between excited quinone and oxygen results in covalent bond formation. Subsequent rearrangement of this intermediate accounts for the results observed.

The interaction of oxygen with electronically excited states of organic molecules can engender many interesting transformations. The most thoroughly studied of these processes is the reaction of a triplet excited state molecule (sensitizer) with oxygen to generate eventually singlet oxygen ($^1O_2$).[2] In recent years it has become apparent that for many photooxygenation reactions the generation of $^1O_2$ represents but a minor reaction path or plays a subsidiary or incidental role in the overall reaction. In a recent report Foote and co-workers[3] suggest that 9,10-dicyanoanthracene sensitizes substrate oxidation through the intervention of superoxide radical anion ($O_2^-\cdot$). The $O_2^-\cdot$ then proceeds to react with the radical cation of the substrate to form products reminiscent of $^1O_2$. Wilson and co-workers[4] have found that photooxidation of cyclooctatetraene with *p*-benzoquinone as sensitizer leads to formation of 1,2,4-trioxanes. It is suggested that this reaction proceeds through a 1,4-biradical formed from the sensitizer and olefin. Interception of this intermediate by oxygen, it is postulated, generates the observed products. Shimizu and Bartlett[5] have reported the results of their studies of photooxidation of olefins using α-dicarbonyl compounds as sensitizers. They find that olefins that normally are unreactive toward $^1O_2$ proceed to form high yields of epoxides (a product generally uncharacteristic of the reaction of $^1O_2$ with olefins). Bartlett[6] has recently communicated the interesting observation that photoepoxidation under these conditions does not lead to the incorporation of an oxygen atom from molecular oxygen in the diketone sensitizer. This finding clearly eliminates many of the most straightforward paths for epoxide formation in this system. Jefford and Boschung[7] have investigated the reaction of biadamantylidene with oxygen and a number of photosensitizers under a wide range of conditions. They report that the mode of oxidation depends critically on the sensitizer. For example, in acetone solvent methylene blue sensitization results in the 1,2-dioxetane in greater than 95% yield; whereas with rose bengal as sensitizer epoxide is formed with a yield of greater than 95%. These workers conclude that at least two unconnected mechanisms are operating in this system. The first is the normal reaction of $^1O_2$ with olefins to form dioxetanes with a small amount of epoxide resulting, perhaps, from reaction of a perepoxide intermediate. The second is a complex path involving as a key step electron transfer from ground state sensitizer to $^1O_2$ to generate $O_2^-\cdot$.

In this report we describe the results of our investigation of the auto-photooxidation of acenaphthenequinone (1) to 1,8-naphthalic anhydride (2) and the photooxidation of olefins using quinone 1 as sensitizer. This system presents the opportunity to examine the disposition of oxygen in the reaction products and may provide further insight into the general structural and mechanistic requirements of photooxidation.

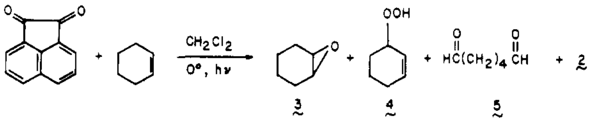


(1)

Results

Irradiation of a CH_2Cl_2 solution of quinone 1 at 0 °C with a constant stream of oxygen flowing through the solution generates cleanly naphthalic anhydride 2 as the only detected product.[8] Anhydride 2 can be isolated by evaporation of the solvent followed by recrystallization in 80% yield. This is similar to the results reported by Mayuyama and co-workers[9] who probed the photooxidation of 1 in THF solvent. We have determined that all three components, the quinone, light, and oxygen, are required for the reaction to proceed.

When quinone 1 was photooxidized in the presence of an olefin, cyclohexene, for example, anhydride 2 was formed again and simultaneously the olefin was converted to a mixture of oxygenated products. For cyclohexene these were identified as: cyclohexene oxide (3), 3-hydroperoxycyclohexene (4) in 33 and 44% yield, respectively, and a small and variable amount of adipaldehyde (5). It was found again that quinone, light, and oxygen are required for the olefin oxidation.



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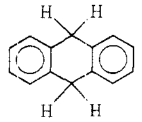
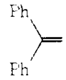
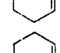
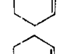
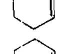
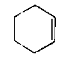
A series of experiments was carried out to define the mechanism for these reactions. We first turn our attention to the oxidation of the quinone to the anhydride in the absence of olefin.

Investigation of the spectroscopic properties of quinone 1 revealed that in carefully purified CH_2Cl_2 at or below room temperature there is an emission with a maximum at 565 nm. This luminescence was identified as phosphorescence by the effect of added quenchers. For example, saturation of the solution with oxygen resulted in the complete quenching of this emission. Phosphorescence from quinone 1 has been observed in rigid media at 77 K to give approximately the same spectrum we observe in fluid solution.[10] There is no detectable fluorescence from quinone 1. We interpret this observation to indicate that the rate of intersystem crossing is rapid. Thus, the bimolecular chemistry of quinone 1 almost certainly originates from the triplet state.

0022-3263/79/1944-0847$01.00/0

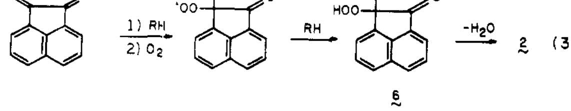
Table I. Effect of Concentration, Wavelength, and Quenchers on the Photooxidation of 1 to Anhydride 2 [a]

[1], M	additive	irradiating wavelength, nm	$\Phi_{ox}^{rel\,b}$
8.8×10^{-5}		315	1.00
1.04×10^{-4}		483	0.82
1.04×10^{-4}	 $(1.16 \times 10^{-3}$ M)	410	0.97[c]
1.04×10^{-4}	 $(3 \times 10^{-3}$ M)	483	0.92
2.64×10^{-5}		315	0.93
6.59×10^{-5}		315	1.11
1.32×10^{-4}		315	0.97
2.64×10^{-4}		315	1.10
5.27×10^{-4}		315	1.00
2.81×10^{-3}	 $(3.95 \times 10^{-3}$ M)	380	1.00[d]
2.81×10^{-3}	 $(1.98 \times 10^{-2}$ M)	380	0.95
2.81×10^{-3}	 $(9.88 \times 10^{-2}$ M)	380	1.06
2.81×10^{-3}	 $(4.94 \times 10^{-1}$ M)	380	1.00

[a] Irradiations were carried out with a 150 W Hg–Xe lamp with a 0.25 M monochromator used for wavelength selection. Bandpass was adjusted to be 10 nm of the central wavelength stated in the table. [b] The absolute quantum yield for photooxidation was determined at 315 and 483 nm to be 0.087 and 0.071, respectively, by comparison with ferrioxolate at 0 °C in CH_2Cl_2 with [1] = 8.8 × 10^{-5} M. [c] Relative to irradiation of an identical solution of 1 at 410 nm but without the addition of the dihydroanthracene. [d] Relative to irradiation of an identical solution of 1 at 380 nm but without the addition of cyclohexene.

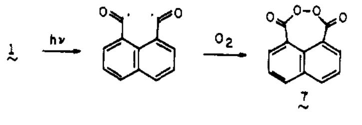
The quantum yield for photooxidation of 1 was determined under a variety of conditions by comparison with ferrioxalate.[11] These results are summarized in Table I. Basically, it was observed that the efficiency of conversion of 1 to anhydride 2 is independent of the irradiating wavelength and, critically, also independent of the concentration of quinone 1. It is important to realize that the quantum yields were determined under conditions of low conversion so that competitive absorption by the product does not complicate the experiment.

Several reactive intermediates can be imagined to precede formation of anhydride 2. Mayuyama and co-workers[9] suggested that the initial step in the oxidation was hydrogen atom abstraction from solvent to form a radical intermediate which reacted sequentially with oxygen and a second hydrogen atom donor (solvent) to form hydroperoxy ketal 6. Loss of water from this intermediate, it was suggested, gives rise to the anhydride, eq 3. To test this mechanism we carried out the oxidation reaction in the presence of the very good hydrogen atom donor, 9,10-dihydroanthracene (DHA).[12] As can be seen from the data presented in Table I, the addition of 1 × 10^{-3} M DHA did not result in a significant increase in the efficiency of photooxidation of 1. This observation, coupled with the observation of phosphorescence in CH_2Cl_2, effectively rules out any mechanism which requires hydrogen atom transfer to be in competition with other fast unimolecular reactions under our conditions.



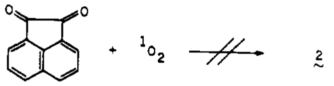
(3)

Another possible mechanism for the conversion of quinone 1 to anhydride 2 is a Baeyer–Villiger type oxidation of the quinone by an intermediate diacyl peroxide. The peroxide could be formed by the trapping of the biradical resulting from α cleavage of the quinone with oxygen, eq 4.[13] To test this possibility we sought to prepare and isolate peroxide 7 by a series of different routes. Unfortunately, they were all spectacularly unsuccessful. However, we attempted to model the reaction of 7 with 1 by the use of phthaloyl peroxide (8).[14] Reaction of an equimolar solution of quinone 1 and peroxide 8 at room temperature for 12 h did not give rise to any anhydride 2.



(4)

We expected that quenching of triplet 1 by oxygen would give rise to some $^1O_2$. This expectation was borne out by experiment (see below). To examine the possibility that $^1O_2$ is responsible for the conversion of 1 to 2, we investigated the behavior of 1 in the presence of $^1O_2$. Irradiation of methylene blue (MB) in the presence of oxygen has been shown to be an uncomplicated source of $^1O_2$.[7] When a solution of 1 and MB in CH_2Cl_2 is irradiated at wavelengths above 600 nm (only MB absorbs), no conversion to 2 is obtained. This finding clearly rules out the direct conversion of 1 to 2 by $^1O_2$.



(5)

Another possible route for the conversion of 1 to 2 involves the generation of $O_2^-\cdot$ by electron transfer from excited quinone. The oxidation potential of the quinone excited state is reduced by the amount of the excitation energy when compared to the ground state. Thus, electron transfer processes may compete effectively with other decomposition paths available to the excited state. Several diagnostic reagents have been developed to detect the presence of $O_2^-\cdot$ in solution. Tetranitromethane reacts with $O_2^-\cdot$ at nearly the diffusion limited rate to form NO_2 and the strongly absorbing nitroform anion.[15] Nitrotetrazolium blue dication is reduced by $O_2^-\cdot$ to form its highly colored diformazan.[16] Incorporation of either of these indicators in solutions of quinone 1 did not demonstrate the formation of $O_2^-\cdot$ during irradiation. This finding, of course, does not rule out the possibility that a cage ion pair is formed which efficiently goes on to products. However, this result does indicate that free $O_2^-\cdot$ is not involved in the oxidation of the added olefins (see below).

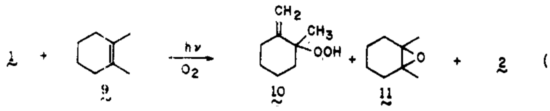
The concomitant oxidation of olefins during the conversion of 1 to 2 offers the opportunity to probe further the mechanism for the quinone oxidation and presents a system for the examination of the interaction of olefins with nπ* type oxygen sensitizers. A series of experiments designed to define the transformations involved in this system was carried out.

The quenching of the phosphorescence of quinone by cyclohexene is a relatively inefficient process. We estimate that $k_q\tau$ (the Stern–Volmer slope) is approximately 410 M^{-1}. Thus, cyclohexene competes only inefficiently with oxygen for the excited state of the quinone.[17]

As mentioned above, cyclohexene is converted to a number of oxidized products by the interaction with photoexcited 1 and oxygen. The effect of cyclohexene on the conversion of 1 to anhydride 2 was investigated. Surprisingly, over a range of cyclohexene concentration from ca. 4 × 10^{-3} to 5 × 10^{-1} M the quantum yield for the conversion of quinone 1 to anhydride

2 is completely unaffected by the olefin. Also, addition of 1,1-diphenylethylene does not quench the oxidation of **1**. These data are collected in Table I. The insensitivity of **1** to the presence of olefin indicates that these two reaction paths do not diverge competitively from a common reactive intermediate.

To probe further the olefin oxidation reaction, this transformation was studied with several substrates under different conditions. Inclusion of the radical trap, 2,4,6-tri-*tert*-butylphenol, in the reaction mixture did not change the product yields or ratios. This observation seems to rule out radical chain autoxidation. To confirm this conclusion the oxidation of 1,2-dimethylcyclohexene (**9**) was carried out. This system is particularly convenient because the $^1O_2$ and free radical oxidation products are different.[18] Photolysis of a 3.4×10^{-3} M solution of **9** containing 3.4×10^{-3} M **1** with light greater than 404 nm in CH_2Cl_2 at 0 °C gave rise to 2-hydroperoxy-2-methyl-1-methylenecyclohexylidene (**10**), dimethylcyclohexene oxide **11**, and anhydride **2** in 70, 4, and 68% yield, respectively. Importantly, there is no evidence for formation of any 3-hydroperoxy-1,2-dimethylcyclohexene, the product of free radical oxidation of **9**. The oxidation of cyclohexene **9** under these conditions is apparently occurring by the reaction with $^1O_2$ to generate **10** and by some other path to form epoxide **11**.



(6)

To probe the stereochemistry of epoxide formation the oxidation of *cis*- and *trans*-stilbene was investigated. Photolysis of quinone **1** in the presence of *trans*-stilbene under constant oxygen bubbling led to *cis*-stilbene, *cis*-stilbene oxide, *trans*-stilbene oxide, benzaldehyde, and anhydride **2** in 25, 4.6, 17, 10, and 60% yield, respectively, based on consumed *trans*-stilbene. Oxidation of *cis*-stilbene under the same reaction conditions led to an almost identical product mixture. Evidently there are at least four processes operating in this reaction system. The first is photosensitized trans to cis isomerization of stilbene. The triplet energy of the quinone dictates that the photostationary state from this reaction will contain predominantly the cis isomer.[19] The second process is the oxidation of quinone to anhydride. The third is the reaction of $^1O_2$ with *cis*- or *trans*-stilbene to generate benzaldehyde.[20] The last is the formation of the stilbene oxides. This last reaction evidently is nearly completely nonstereoselective. Since starting with *cis*-stilbene gives the same ratio of oxides as starting with *trans*-stilbene, this observation indicates that the epoxidation of the olefins is most likely a stepwise process.

Discussion

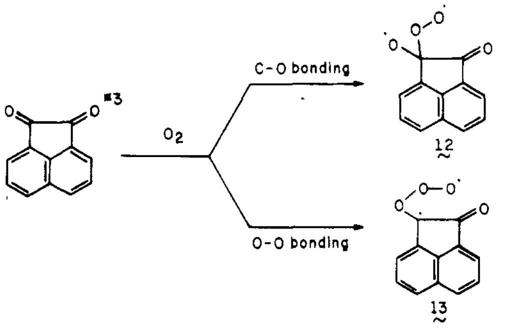
Our investigation of these photooxidation reactions has revealed a quite complex system. Our findings do not lead to an inexorable mechanistic conclusion. However, it is clear that several possible mechanisms are not operating and we can propose a mechanism that is consistent with our experimental findings.

The most telling experiments are those that reveal the quantum efficiency for oxidation of **1** to anhydride **2** to be independent of the quinone concentration and the presence of olefin. These findings indicate that only one quinone molecule is oxidized for every oxygen molecule consumed. If an oxidized intermediate was capable of converting a second quinone molecule to anhydride and also oxygenating olefin to epoxide, then the presence of olefin should have an inhibitory effect on the oxidation of quinone. Likewise, if an oxidized intermediate could either decay or transform a molecule of quinone to the anhydride, a dependence on quinone concentration would be expected. Moreover, these results indicate that the olefin competes only ineffectively with oxygen for the triplet excited state of the quinone as is evidenced by the relatively small value of $k_q\tau$.

We suggest that the initiating step in the reaction path leading to epoxide and quinone is bond formation between the excited quinone and oxygen. A priori, there are two reasonable sites for oxygen bonding to excited quinone **1**, the carbonyl carbon and the carbonyl oxygen. The detection of phosphorescence from **1** at room temperature leads us to agree with the assignment of predominant $n\pi^*$ character for the lowest triplet of quinone **1**.[10] For $n\pi^*$ carbonyl compounds, the oxygen atoms tend to be electrophilic while the π system behaves as a nucleophile.[21] For this reason the initial reaction might be carbon–oxygen bond formation to form the peroxy–alkoxy biradical intermediate **12**. However, we cannot rule out, and tend to favor, formation of the trioxide biradical **13**, eq 7. Alkyl trioxides are in fact reasonably well characterized and have been detected in a number of systems.[22] Indeed, an intermediate similar to trioxide **13** is capable of explaining the labeling results reported by Bartlett[6] if the active oxygen atoms are transferred one at a time to olefin molecules.

Whichever intermediate is in fact formed, our results indicate that it is not capable of oxidizing quinone to anhydride under our reaction conditions. Consider first the possible fate of **12**. It is clear that this intermediate must at some time during the reaction insert one oxygen atom between the bridging carbons and lose one oxygen atom. The sequence of these events is not revealed by our experiments. One reasonable possibility, however, is rearrangement of **12** to what is essentially a carbonyl oxide, intermediate **14**, perhaps in one step or through an intermediate such as **15**, eq 8. Attempts to trap intermediate **14** as an ozonide with added acetaldehyde were unsuccessful.

Loss of oxygen from **14** will yield the anhydride **2**. In the presence of olefin, the active oxygen of **14** would be transferred



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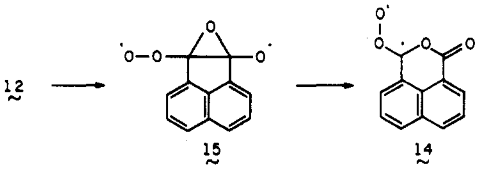

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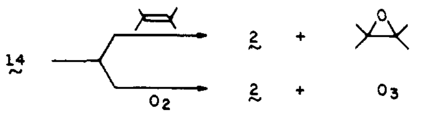

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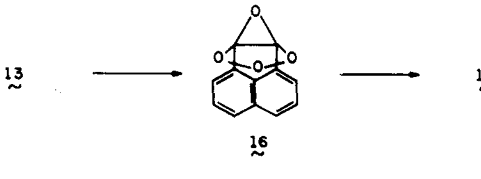

(10)

to form the epoxide. This reaction is expected to be nonstereospecific if the transfer is stepwise. Oxygen atom transfers have been postulated to occur from the peroxide intermediates formed during ozonolysis of alkynes.[23] In the absence of olefin, loss of oxygen from **14** does not oxidize a second quinone. One possible pathway is the donation of an oxygen atom from **14** to an oxygen molecule to generate ozone, eq 9.

We have no direct evidence for the formation of ozone; it is interesting to note, however, the formation of adipaldehyde from the cyclohexene oxidation, a product not reported to result from the reaction of $^1O_2$ with this olefin, but one that may result from the ozonolysis.[24] Moreover, this product is observed only at low olefin concentration where competition between epoxide formation and generation of ozone might permit the latter reaction to occur.

Finally, it should be noted that a similar reaction sequence can be postulated if trioxide intermediate **13** results from the interaction of excited **1** with oxygen. However, in this case intermediate **16** (analogous to **15**) would undergo two-bond cleavage to form **14**, eq 10. The rearrangement of **16** to **14** is exactly the well precedented reaction of a primary ozonide to the Criegee intermediate.[25]

Competing with the oxidation of triplet **1** is energy transfer to ground state oxygen to form $^1O_2$. In the absence of olefin the $^1O_2$ returns to the ground state and this path simply represents a route for energy wastage. In the presence of olefin the $^1O_2$ reacts to form primarily the hydroperoxide products observed.

One final point to be disucssed is the relationship of this system and proposed mechanism to that discovered by Bartlett and co-workers.[5] The major difference is the fate of the sensitizer. It is tempting to speculate that, at least for benzil and biacetyl sensitizers, the trioxide intermediate analogous to **13** is formed exclusively. Transfer of one oxygen atom sequentially to two olefin molecules can explain the labeling study and will regenerate the diketone. The question that remains to be answered concerns the lack of cyclization of these intermediates to analogues of **16**. The most reasonable explanation centers on the constrained five-membered ring of **13**. Perhaps entropic factors mitigate against rapid cyclization in the acyclic cases and, at high olefin concentration, oxygen atom transfer to form epoxide occurs exclusively.

In summary, the reaction sequence outlined in 7–10 represents a plausible sequence of events for the oxidation of **1** and olefins that is consistent with the known experimental observations. Further work on this apparently general photooxidation scheme is underway.

Experimental Section

General. All melting points were corrected according to the melting point (80.1 °C) of sublimed naphthalene. NMR spectra were recorded on a Varian Associates EM-390 instrument with tetramethylsilane as internal standard. Gas chromatographic analysis was carried out on a Varian Associates 2700 all glass chromatograph with a 6 ft × 0.25 in., 3% SE-30 column. Absorption spectra were recorded on a Perkin-Elmer Model 202 spectrophotometer or a Cary 14 instrument. Emission spectra were recorded on a Farrand Mark I spectrofluorimeter. Irradiation was carried out on a preparative scale using a Hanovia 450 W medium pressure Hg arc lamp cooled in a water jacketed Pyrex well. The well was covered with tape to block light emission over all but an approximately 1 in. opening. Wavelength selection was achieved by placing the appropriate Corning color glass filter in the light path. The light was then focused on the reaction vessel which was maintained at constant temperature by means of an external cooling source. Irradiation on an analytical scale was carried out using the excitation optics of the Farrand spectrofluorimeter. Wavelength selection was achieved with the excitation monochromator with 10 nm bandpass slits in both the entrance and exit ports. The concentration of anhydride **2** was monitored spectroscopically at 340 nm, a wavelength at which the quinone **1** is nearly transparent.

Purification of Acenaphthenequinone (1). Technical grade quinone (Aldrich Chemical Co.) was purified by chromatography on silica gel with CH_2Cl_2 followed by repeated recrystallization from CH_2Cl_2 to give long yellow needles (mp 250–253 °C dec). The best criterion for purity was the phosphorescence emission spectrum in CH_2Cl_2 at room temperature. In general, samples of **1** were recrystallized until further recrystallization led to no further changes in the intensity of the phosphorescence.

Photolysis of Quinone 1. (a) In the Absence of Olefin. A solution of quinone (50 mg, 0.28 mmol) in 100 mL of freshly distilled CH_2Cl_2 was prepared and purged with O_2 at 0 °C. The solution was irradiated as described above using a CS-3-73 filter with constant O_2 bubbling for 4 h. Evaporation of the solvent in vacuo gave a solid which was recrystallized from CH_2Cl_2 to give 43 mg (80%) of an off-white solid identified as 1,8-naphthalic anhydride by comparison with an authentic sample (Aldrich Chemical Co.).

(b) With Cyclohexene. A solution of **1** (42 mg, 0.2 mmol) and freshly distilled cyclohexene (19 mg, 0.23 mmol) was prepared in 60 mL of CH_2Cl_2. The solution was irradiated as described in part (a) above for 5.5 h. Analysis of the photolysis solution by gas chromatography revealed cyclohexene oxide (33%, by comparison with an authentic sample). Analysis of the NMR spectrum revealed hydroperoxide **4** in ca. 40% yield identified by comparison with an authentic sample[24] and adipaldehyde.[26] Evaporation of the solvent and crystallization gave anhydride **2** in 65% isolated yield. An identical experiment, except that 2,4,6-tri-*tert*-butylphenol (2.99 mg, 0.011 mmol) was included in the photolysis solution, gave the same product mixture.

(c) With 1,2-Dimethylcyclohexene (9). The dimethylcyclohexene was prepared by the procedure of Signaigo[27] and purified by preparative gas chromatography. A solution of **1** (49.5 mg, 0.27 mmol) and **9** (30 mg, 0.272 mmol) was prepared in 60 mL of CH_2Cl_2 and irradiated for 5 h as described above. Gas chromatographic analysis of the reaction solution revealed epoxide **11** in 4% yield (based on starting **9**). Analysis by NMR showed a 70% yield of hydroperoxide **10**. Neither NMR nor GC analysis showed any evidence for 3-hydroperoxy-1,2-dimethylcyclohexene. We estimate we could have detected 2% of this compound. Evaporation of the solvent and crystallization gave **2** in 68% yield (based on **1**).

(d) With *trans*-Stilbene. A solution of **1** (43 mg, 0.23 mmol) and *trans*-stilbene (41.5 mg, 0.23 mmol) in 40 mL of CH_2Cl_2 was irradiated as above. The following products were identified and quantitated by gas chromatographic comparison with authentic samples (yields are based upon starting *trans*-stilbene): *cis*-stilbene, 25%; *cis*-stilbene oxide, 4.6%; *trans*-stilbene oxide, 17%; benzaldehyde, 10%. Evaporation of the solvent and crystallization gave anhydride **2** in 60% yield. In an experiment with *cis*-stilbene (44 mg, 0.24 mmol), a virtually identical mixture of products was obtained.

Acknowledgment. This work was supported in part by the Office of Naval Research, in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and in part by the National Science Foundation.

Registry No.—**1**, 82-86-0; **2**, 81-84-5; **3**, 286-20-4; **4**, 4845-05-0; **9**, 1674-10-8; **10**, 54683-51-1; **11**, 17612-36-1; cyclohexene, 110-83-8; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; *cis*-stilbene oxide, 1689-71-0; *trans*-stilbene oxide, 1439-07-2; benzaldehyde, 100-52-7.

References and Notes

(1) Fellow of the Alfred P. Sloan Foundation, 1977–79.

(2) For leading references see: R. W. Denny and A. Nickon, *Org. React.*, **20**, 133 (1973).

(3) J. Ericksen, C. S. Foote, and T. L. Parker, *J. Am. Chem. Soc.*, **99**, 6455 (1977).

(4) R. M. Wilson, E. J. Gardner, R. C. Elder, R. H. Squire, and L. R. Florian, *J. Am. Chem. Soc.*, **96**, 2955 (1974).

(5) N. Shimizu and P. D. Bartlett, *J. Am. Chem. Soc.*, **98**, 4193 (1976).

(6) (a) P. D. Bartlett in "Organic Free Radicals", W. A. Pryor, Ed., American Chemical Society, Washington, D.C., 1978, p 15; (b) P. D. Bartlett and J. Becherer, *Tetrahedron Lett.*, 2983 (1978).

(7) C. W. Jefford and A. F. Boschung, *Helv. Chim. Acta*, **60**, 2673 (1977).

(8) The NMR spectrum of the crude photolysis mixture shows only **2**.

(9) K. Maruyama, K. Ono, and J. Osugi, *Bull. Chem. Soc. Jpn.*, **45**, 847 (1972).

(10) A. Kuboyama and S. Yabe, *Bull. Chem. Soc. Jpn.*, **40**, 2475 (1967).

(11) J. G. Calvert and J. N. Pitts in "Photochemistry", Wiley, New York, 1966, pp 783–786.

(12) T. Matsaura and Y. Ito, *Bull. Chem. Soc. Jpn.*, **47**, 1724 (1974); S. Korcek, J. H. B. Chenier, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **50**, 2285 (1972).

(13) M. J. Bruce, *Chem. Quinonoid Compd.*, *Part 1*, 465 (1974).

(14) F. D. Greene, *J. Am. Chem. Soc.*, **78**, 2246 (1956).

(15) B. H. J. Bielski and A. O. Allen, *J. Phys. Chem.*, **71**, 4544 (1967).

(16) R. W. Miller and C. T. Kerr, *J. Biol. Chem.*, **241**, 5597 (1966).

(17) Quenching of the quinone triplet by O$_2$ is expected to be diffusion limited which in CH$_2$Cl$_2$ corresponds to a bimolecular rate constant of ca. 1 × 10^{10} M^{-1} s.
(18) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
(19) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **84**, 4983 (1962).
(20) G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, 3555 (1971).
(21) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 1318 (1970).
(22) J. E. Bennet, D. M. Brown, and B. Mile, *Trans. Faraday Soc.*, **66**, 397 (1970); P. D. Bartlett and M. Lahav, *Isr. J. Chem.*, **10**, 101 (1972); P. E. Story, D. E. Emge, and R. W. Murray, *J. Am. Chem. Soc.*, **98**, 1880 (1976); F. Kovac and B. Plesnicar, *J. Chem. Soc., Chem. Commun.*, 122 (1978).
(23) R. E. Keay and G. A. Hamilton, *J. Am. Chem. Soc.*, **98**, 6578 (1976); N. C. Yang and J. Libman, *J. Org. Chem.*, **39**, 1782 (1974).
(24) K. Kopecky and H. Reich, *Can. J. Chem.*, **43**, 2265 (1965).
(25) P. S. Bailey in "Ozonation in Organic Chemistry", Vol. 1, Wiley, New York, 1978.
(26) J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966).
(27) F. K. Signaigo and P. L. Cramer, *J. Am. Chem. Soc.*, **55**, 3326 (1933).

Differentiation in Singlet Oxygenation Rates of 2,3-Diaryl-2-butenes as a Function of Cis–Trans Isomerism[1]

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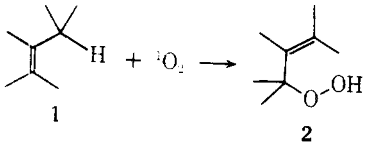
Received October 11, 1978

The photosensitized singlet oxygenation of *cis*- and *trans*-2,3-diaryl-2-butenes, including the 2,3-diphenyl (**1a**), 2,3-di-β-naphthyl (**1b**), and 2,3-di-α-naphthyl (**1c**) derivatives, was undertaken. The corresponding 2,3-diaryl-3-hydroperoxy-1-butenes **2a–c** were obtained in essentially quantitative yield and their structures confirmed by iodometry and ^{1}H NMR and IR spectral data. Relative singlet oxygenation rates show that for all cis–trans isomer pairs the cis isomer undergoes ene reaction ca. ninefold faster than the corresponding trans isomer. The greater singlet oxygenation reactivity of the cis isomer in each cis–trans pair correlates well with the first ionization potentials determined by photoelectron spectroscopy in that the more reactive cis isomer has the lower IP (~0.20 eV) for each cis–trans pair. These results are rationalized in terms of the higher steric strain for the more crowded cis isomer.

The chemistry of singlet oxygenation is now well defined, although numerous mechanistic aspects still remain to be resolved in order to understand the details of this important reaction.[3] This applies especially to the classical ene reaction (eq 1) in which an olefinic substrate **1** bearing allylic hydrogens



(1)

1 **2**

is converted into an allylic hydroperoxide **2**. For example, a recent paper accentuates the substrate reactivity problem by determining the rates of the ene singlet oxygenation of a large collection of diverse alkenes.[4] Thus, the greater the degree of alkylation of the ethylenic bond, the faster the rate of singlet oxygenation, correlating satisfactorily with the lower ionization potentials of the more alkylated substrates.[5] However, the situation is more complex since steric, conformational,[3,6] and ring-strain factors[7] play important roles.

We have been interested in preparing allylic hydroperoxides **2** without allylic hydrogens in order to cycloperoxymercurate them to the corresponding mercury-substituted 1,2-dioxetanes **3**.[8] For this purpose we decided to singlet oxygenate cis–trans mixtures of 2,3-diphenyl-2-butenes **1a** to prepare the desired allylic hydroperoxides **2a**. Much to our surprise we observed that *cis*-2,3-diphenyl-2-butene (**1a**) reacted much faster with singlet oxygen than the trans isomer. To the best of our knowledge only limited and inconclusive data have been reported[10] on the relative reactivity of cis–trans isomers toward singlet oxygen.

It was, therefore, of interest to determine the generality and the factors that influence this novel effect.

Results and Discussion

Besides the cis–trans isomers of 2,3-diphenyl-2-butene (**1a**), we investigated the singlet oxygenation of 2,3-di-α-naphthyl- and 2,3-di-β-naphthyl-2-butenes, respectively **1b** and **1c**. These olefins were prepared by the titanium trichloride–lithium aluminum hydride coupling reaction of the corresponding aryl methyl ketones.[9] Separation into the pure cis and trans isomers was achieved by means of repetitive dry column chromatography on silica gel. The unknown α-naphthyl and β-naphthyl systems were characterized on the basis of elemental analysis, mass spectra, and IR and NMR spectral data. The results are summarized in Table I.

Photosensitized oxygenation of the isomerically pure 2-butenes **1** in CCl$_4$ and tetraphenylporphyrin (TPP) as sensitizer afforded the corresponding allylic hydroperoxides **2** in essentially quantitative yield. These unknown substances exhibited the characteristic ^{1}H-NMR and IR spectra. Iodometric titration indicated higher than 95% purity. The results are summarized in Table II. It proved difficult to isolate these highly sensitive hydroperoxides since evaporation of the solvent even at subambient temperatures induced rearrangement and decomposition.

The relative singlet oxygenation rates were determined as described previously[10] by following the consumption of the 2-butene **1** substrate and/or the appearance of the hydroperoxide product **2** in the ^{1}H NMR, using the competition technique. For the most reactive substrate, *cis*-**1a**, we employed tetramethylethylene (TME) and for the least reactive, *trans*-**1c**, cyclooctene as internal standard. The remaining substrates were run against each other, i.e., always in pairs in descending order of the reactivity scale. Fortunately the methyl resonances of the substrate, product, and standard and the vinyl resonances of the product and standard were well

0022-3263/79/1944-0851$01.00/0