by GC (column a) consisted of unreacted **1b**, **6**, **8b**, **9b**, **2b**, and the cyclopentenols derived from **3b** in comparable yields to the pentane photolysis described above.

Photolysis of 1b in Pentane/Methanol. A 0.05 M solution of **1b** in pentane/methanol (100:1) was irradiated with the 10-W Osram lamp for 5 h. GC analysis (column a) of the yellow photolysate indicated the presence of methyl acetate in 1–2% yield.

Photolysis of 1c. A 0.02 M solution of **1c** was irradiated as described above. GC analysis indicated the formation of **6** (7%), *cis*- and *trans*-**8c** (10%), and **9c** (5%). The yields were calculated by taking deuterium scrambling of the starting material (see below) into account but are not corrected for 254-nm products. Alkynone **6** was isolated and analyzed by infrared and mass (10-eV) spectroscopy. The ratio of intensities of the ν(C≡C—H) = 3295 cm^{-1} and ν(C≡C—D) = 2600 cm^{-1} peaks in the IR spectrum was ≡C—H/≡C—D = 12.0. The soft-ion mass spectrum contained four peaks in the molecular ion region: 95:96:97:98 = 100:17.7:4.9:1.4, as compared to the same region in the corresponding spectrum of undeuterated **6** (95:96:97 = 100:10.4:1.4). Starting material was isolated after photolysis and its ^{2}H NMR spectrum examined. The inverse gate decoupled spectrum showed three singlets at δ 2.28, 4.99, and 5.85 in the ratio 1:8:1. Photolysis of a 0.02 M solution of **1c** at 254 nm leads only to the formation of oxetanes. Examination of reisolated starting material by deuterium NMR showed that no detectable scrambling of deuterium had occurred.

Photolysis of 1d. Irradiation of a 0.05 M solution was carried out as described above. Non-volatile products amounted to 27% (0.056 g from 1.117 g of **1d**; 31% conversion). Separation of volatile materials by GC (column a) gave **7** (3%) and **8d** (9%), identified on the basis of its spectral properties:[29] IR (CCl_4) 1715 (s), 1380 (m), 1358 (m), 1157 (m); ^{1}H NMR (CCl_4) δ 1.58 (br s, 3 H), 1.80 (br s, 3 H), 2.10 (s, 3 H), 3.04 (d, 2 H), 5.12–5.53 (m, 1 H); MS, M/e 43 (100), 41 (73), 27 (29), 39 (29), 69 (18), 112 (5). Alkynone **6** could not be detected in the photolysis mixture. Also present were the oxetane **2d**, identified by comparison of its spectral data with those published,[4d] and cyclopentenols arising from GC decomposition of oxetane **3d**.[4d] These products were also present in a 254-nm photolysate, run under the same conditions as above. The rate of formation of **2d** in the 254 nm was 58% as great as that obtained with the unfiltered lamp. The yield of nonvolatile products was <2%.

Photolysis of 1-Octene. A 0.05 M solution of 1-octene was irradiated as described above. Analysis by gas chromatography (column c) showed three products (not isolated) in yields of 32%, 16%, and 6%. The mass spectra of these products showed them to be isomers of the starting material. GC analysis using column a demonstrated the production of 1-octyne in 18% yield, the identity of which was established by comparison of its GC retention times (columns a and c), infrared, and mass spectra with those of an authentic sample.

Acknowledgment. We gratefully acknowledge the technical assistance of Mr. R. Fern in the measurement of the ultraviolet absorption spectra and Dr. J. Reimer for his assistance in measuring the ^{2}H NMR spectra and thank the Department of Chemistry, University of Connecticut at Storrs, for the soft-ion mass spectra.

Registry No. *cis*-**1a**, 4535-61-9; *trans*-**1a**, 1071-94-9; **1b**, 109-49-9; **1c**, 82065-02-9; **1d**, 3240-09-3; **4**, 21889-88-3; **5a**, 61675-14-7; **5c**, 82065-03-0; **6**, 2550-28-9; **6** 2,4-DNP, 82065-04-1; **7**, 22592-18-3; *cis*-**8b**, 51024-76-1; *trans*-**8b**, 763-92-8; *cis*-**8c**, 82065-05-2; *trans*-**8c**, 82065-06-3; **8d**, 28332-44-7; **9b**, 4160-75-2; **9c**, 82080-59-9; **10**, 82065-07-4; (3-(2-methyl-1,3-dioxan-2-yl)propyl)triphenylphosphonium bromide, 82065-08-5; 1,1-dideuterio-4-(2-methyl-1,3-dioxan-2-yl)but-1-ene, 82065-09-6; ethyl acetoacetate, 141-97-9; 3-chloro-2-methylpropene, 563-47-3; 1-octene, 111-66-0; 1-octyne, 629-05-0.

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Laser Photochemistry: Trapping of Quinone–Olefin Preoxetane Intermediates with Molecular Oxygen and Chemistry of the Resulting 1,2,4-Trioxanes[1]

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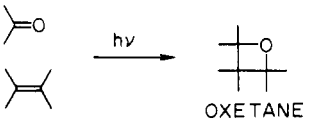
Abstract: The output of an argon ion laser has been used to generate reactive intermediates through the excitation of a carbonyl compound (*p*-benzoquinone or benzophenone) in the presence of an olefin. These reactive intermediates can be trapped either with oxygen to form 1,2,4-trioxanes or with sulfur dioxide to form cyclic sulfones. Several lines of evidence are presented that indicate that these reactive intermediates frequently are not the preoxetane biradicals but instead are charge-transfer exciplex species. Trioxane chemistry has been studied under a variety of conditions and found to be characterized by a fragmentation of the trioxane ring into three carbonyl compounds: the carbonyl compound involved in the formation of the trioxane ring and the two carbonyl compounds formally derived from the oxidative cleavage of the original olefin. The photolability of vitamin K analogues has been established to arise from the initial formation of an intramolecular trioxane with visible light and the fragmentation of this trioxane into the three carbonyl constituents with ultraviolet light.

During the past few years, photochemists have become increasingly aware of the influence of various chemical agents upon the fate of biradical or biradicaloid species. Biradical trapping agents that have been studied in detail to date include molecular oxygen[2] and other paramagnetic species including nitroxyl radicals[3] and nitric oxide,[4] radical scavengers such as di-*tert*-butyl selenoketone[5] and sulfur dioxide,[6] electron acceptors such as paraquat

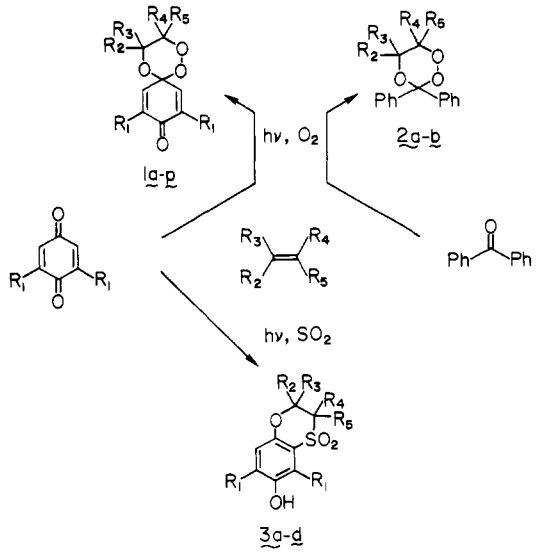
Scheme I



(1) This paper is dedicated to the memory of Robert Burns Woodward, deceased July 8, 1979.

0002-7863/82/1504-4429$01.25/0

Scheme II



salts,[7] hydrogen-donating agents such as hydrogen bromide,[8] thiols,[9] and organic solvents with readily abstractable hydrogen atoms,[10] phosphorus(V) compounds,[11] and even olefins in special cases.[12] In much of this work, the trapping reactions have been studied from a physical standpoint. In these cases, the primary purpose of the work has not been the identification and characterization of the trapping products. However, a number of instances of the isolation of biradical trapping products now have been reported. Thus, trapping with molecular oxygen often leads to peroxide formation,[2a,b,d,e,g,k-o] with selenoketones to selenides,[5] with sulfur dioxide to sulfones,[6] and with olefins to a variety of new carbon skeletons.[12a-e] These trapping results demonstrate that biradicals undergo reactions other than the usual self-annihilation processes; they demonstrate that biradicals may be manipulated with external reagents in much the same fashion as the less ephemeral intermediates of organic chemistry: radicals, carbocations, and carbanions.

One of our main interests in this area has been the development and application of biradical trapping techniques to the Paterno–Büchi reaction, the photochemical cycloaddition between excited carbonyl compounds and olefins to form oxetanes (Scheme I). In particular, we have concentrated upon molecular oxygen as a trapping agent and sought to develop the biradical trapping approach as a synthetically useful peroxide synthesis[2b,d,e,g] and as a method for probing the nature of the transient species being trapped.[21] In this paper our studies with the Paterno–Büchi reaction are described in detail.

Biradical Trapping Procedures. Two biradical trapping agents have been found to be particularly effective in intercepting the Paterno–Büchi intermediates; these are molecular oxygen and sulfur dioxide. The molecular oxygen trapping reaction produces 1,2,4-trioxanes **1a–r** or **2a,b** depending upon whether the carbonyl constituent is *p*-benzoquinone or benzophenone, respectively (Scheme II). On the other hand, sulfur dioxide trapping leads to rearranged sulfones **3a–d** (vide infra) (Scheme II). The reaction conditions and results of all successful trapping reactions studied to date are summarized in Table I. Of these two trapping procedures, the application of molecular oxygen has been studied much more extensively.

Synthesis of 1,2,4-Trioxanes

Effect of Light Wavelength. In our initial work with *p*-benzoquinone and cyclooctatetraene,[2b,d] trioxane formation was found to occur most readily in an inert solvent, under an atmosphere of oxygen and with the visible output of an argon ion laser.[13] It was observed in this system and in other *p*-benzoquinone systems studied subsequently that the dienone trioxanes **1a–r** were extremely photolabile and to a lesser degree thermally labile. Therefore, it is crucial to the success of the trapping reaction that the stimulating light be absorbed only by the *p*-benzoquinone and that no ultraviolet light be present that would be absorbed by the dienone chromophore in the product trioxanes.[14] Thus, when a conventional photochemical light source, such as a Rayonet photochemical reactor with 350-nm lamps, is used (cyclooctatetraene, Table I), extremely complex reaction mixtures result. These mixtures do contain trioxanes, but they are present in such low yields and obscured by so many other products that the only way that they can be isolated is by thick-layer chromatography vs. a tracer sample of the pure trioxane. Substantial increases in the yields of trioxanes are realized with the output of a 1000-Watt Xe–Hg arc that has been filtered to eliminate the ultraviolet wavelengths. Unfortunately, this filtration process so greatly reduces the visible light intensity that reaction times can become excessively long and the thermal decomposition of the trioxane often becomes significant. The first two entries under olefin 13 in Table I illustrate this point. With the filtered output of a 1000-W Xe–Hg arc a 36% yield of trioxane **1p** was obtained after 24 h of irradiation, whereas the same amount of starting material afforded a 54% yield of **1p** after only about 1 h of irradiation with all of the visible lines of a 4-W argon laser. Thus, the argon laser has been found to be the ideal source for these *p*-benzoquinone reactions, since it provides a high light intensity in the blue–green region of the spectrum that is not contaminated with undesired ultraviolet wavelengths. Furthermore, with the recent availability of an 18-W argon laser, it has become possible to obtain single lines of ultraviolet light[13] with sufficient intensity (1–0.5 W) to produce trioxanes **2a,b** from ketones such as ben-

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(3) Reference 2i and Anderson, D. R.; Keute, J. S.; Koch, T. H.; Moseley, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 6332.

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(6) (a) Farid, S. *J. Chem. Soc.* **1971**, 73. (b) Wilson, R. M.; Wunderly, S. W. *J. Am. Chem. Soc.* **1974**, *96*, 7350. (c) Hamer, N. K. *J. Chem. Soc., Chem. Commun.* **1975**, 557.

(7) References 2h and 2j. (a) Small, R. D., Jr.; Scaiano, J. C. *J. Photochem.* **1977**, *6*, 453. (b) *J. Phys. Chem.* **1977**, *81*, 828. (c) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7108.

(8) O'Neal, H. E.; Miller, R. G.; Gunderson, E. *J. Am. Chem. Soc.* **1974**, *96*, 3351.

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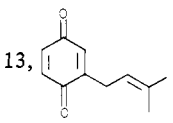
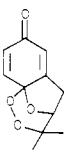
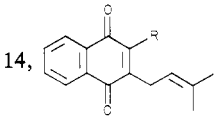
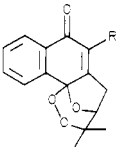
(13) The work described in this paper was initiated with an 8-W argon ion laser. More recently an 18-W argon ion laser has been obtained. These lasers are commercially available from Coherent Radiation. The 18-W laser is particularly useful, since it affords both visible and ultraviolet lines that are sufficiently intense for preparative photochemical work. For further details concerning the characteristics of these lasers see the Experimental Section.

(14) The n,π^* absorption band system of *p*-benzoquinone coincides nicely with the visible output of the argon laser: λ_{max}^{hexane} 479 nm (ϵ = 11) and 458 (21). On the other hand, the dienone chromophore in the trioxanes does not begin to absorb light until below 380–390 nm.

Table I. Reaction Conditions and Yields of Biradical Trapping Reactions to Form Trioxanes 1a–r and 2a,b and Sulfones 3a–d

olefin	substituents[a] R_1	R_2	R_3	R_4	R_5	trapping product: trioxane, %	trapping product: sulfone, %	reaction conditions: light[b] source	oxygen pressure, atm	temp, °C[c]	solvent
1, cyclooctatetraene[d]	H	H	$-(CH=CH)_3-$		H	**1a** (49)		AL (vis)	.23 (air)		CCl_4
						1a (50)		AL (vis)	1		CCl_4
						1a (0)		AL (vis)	.23 (air)		AcOH
						1a (4)		Ray (350)[e]	.23 (air)		CCl_4
2, styrene	H	H	H	H	Ph	**1b** (56)		AL (vis)	1	<20	CCl_4
						1b (25)		AL (vis)	1	<20	CH_3CN
						1b (94)		AL (vis)	12		CCl_4
	CH_3	H	H	H	Ph	**1c** (40)		AL (488)	11		CCl_4
3, 1,1-diphenylethylene	H	H	H	Ph	Ph	**1d** (42)		AL (vis)	1	<20	CCl_4
4, tetramethylallene	H	$=C(CH_3)_2$		CH_3	CH_3	**1e** (40)		AL (vis)	11		CCl_4
5, 1,1-dicyclopropylethylene	H	H	H		c-C_3H_5	**1f** (49)		AL (488)	13	−10	CCl_4
6, *tert*-butylethylene	H	H	H	H	*t*-Bu	**1g** (25)		AL (vis)	1	<20	CCl_4
						1g (66)		AL(vis)	11		CCl_4
							3a (81)	AL (vis)		−11	20% SO_2, CCl_4
7, cyclohexene	H	H	$-(CH_2)_4-$		H	**1h** (29)		AL (vis)	1	<20	CCl_4
						1h (58)		AL (vis)	11		CCl_4
							3b (58)	AL (vis)		−11	20% SO_2, CCl_4
	CH_3	H	$-(CH_2)_4-$		H	**1i** (58)		AL (vis)	12		CCl_4
		H	$-(CH_2)_4-$		H	**2a** (10)		AL (UV)	12		CCl_4
8, cyclooctene	H	H	$-(CH_2)_6-$		H	**1j** (13)		AL (vis)	11		CCl_4
9, norbornene	H	H			H	**1k** (20)		AL (488)	13	−10	CCl_4
		H			H	**2b** (45)[f]		Xe-Hg[g]	11		$CFCl_3$
10, vinyl acetate	H	H	H	H	OAc	**1l** (dec)		AL (vis)	11		
	H	H	H	H	OAc		**3c** (20)	AL (vis)		−11	20% SO_2, CCl_4
	H	OAc	H	H	H	**1m** (18)		AL (vis)	11		CCl_4
	H	OAc	H	H	H		**3d** (16)	AL (vis)		−11	20% SO_2, CCl_4
11, 2,2-dimethyl-3-(trimethylsiloxy)-3-butene	H	H	H	*t*-Bu	$OSi(CH_3)_3$	**1n** (66)		AL (vis)	11		CCl_4
12, 1-phenyl-1-(trimethylsiloxy)ethylene	H	H	H	Ph	$OSi(CH_3)_3$	**1o** (78)		AL (vis)	11		CCl_4
13, 						**1p** (36)		Xe-Hg[g]	11		CCl_4
						1p (54)		AL (vis)	11		CCl_4
						1p (98)		AL (vis)	11	−80	$CFCl_3$
14, 						R = CH_3; **1q** (35)		AL (457.9)	12	−30	$CFCl_3$
						R = OCH_3; **1r** (26)		AL (457.9)	12	−30	$CFCl_3$

[a] See Scheme II. [b] The code for the various light sources is as follows: AL, argon laser; Ray, Rayonet photochemical reactor; Xe-Hg, 1000-W Hanovia Xe-Hg source. The number in parentheses is the wavelength of light used in the experiment in nm; (vis) all visible lines and (UV) all ultraviolet lines of the argon laser. [c] Room temperature unless otherwise stated. [d] Wilson, R. M.; Gardner, E. J.; Elder, R. C.; Squire, R. H.; Florian, L. R. *J. Am. Chem. Soc.* 1974, *96*, 2955. [e] Broad spectrum lamps with output maximum at ~350 nm and emission down to ~310 nm. [f] Based on recovered starting material; see Experimental Section. [g] Lamp output filtered; see Experimental Section.

zophenone that absorb in the 350-nm region (olefins 7 and 9, Table I).

Effect of Oxygen Pressure. Another parameter that has a substantial effect upon the trioxane yield is the oxygen pressure. We routinely conduct irradiations under oxygen pressures of up to 15 atm in Griffin–Worden tubes (Kontes) (Figure 1A). However, it is emphasized that in order to minimize the risk of explosion, high-pressure oxygen experiments are conducted with use of only noncombustible solvents such as carbon tetrachloride or Freon-11 ($CFCl_3$). Thus, by increasing the oxygen pressure from 1 atm to about 11 atm, it is often possible at least to double the trioxane yield (olefins 2, 6 and 7, Table I).

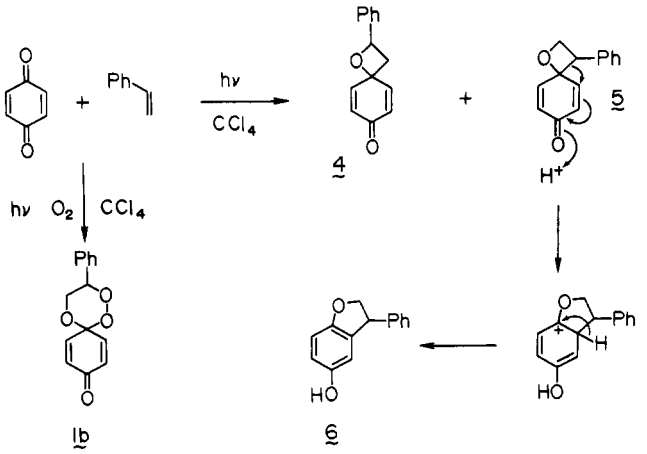
In an effort to obtain more quantitative information bearing upon the effects of oxygen pressure, a prototype relative quantum yield device was constructed. This device was designed to permit the use of sample tubes permanently attached to high-pressure oxygen lines and to make the most efficient use of the highly directional and very intense laser source. It is illustrated in Figure 1B and functions by first diverging the laser beam and then sweeping the beam from one sample to the next by means of a rapidly rotating mirror. Thus, instead of rotating the samples about a fixed central light source as is done in the conventional "merry-go-round" quantum yield device, this laser device rotates a central light source about a fixed circular array of samples. This "lighthouse" reactor has only been used in relative yield studies. Reliable quantum yield determinations must await the development of actinometers that can be used at very high light intensities and with these low quantum yield trapping reactions. Nevertheless, the effect of oxygen pressure has been examined in several cases, and the reaction of *p*-benzoquinone with styrene is par-

Table II. The Effect of Oxygen upon the Photochemical Addition of *p*-Benzoquinone to Styrene

oxygen pressure, atm	*p*-benzoquinone consumed, %	yield, %[a] trioxane **1b**	yield, %[a] oxetane **4** + dihydrofuran **6**
10.8	82	94	[b]
1.0	28	41	15
0.2[c]	18	19	10
0.0	12	0.0	8

[a] These values represent isolated yields based upon starting material consumed. [b] A small amount (5 mg) of nontrioxane product was isolated, but this was not enough material to determine oxetane and dihydrofuran yields. [c] Air.

Scheme III



ticularly interesting in this respect (Scheme III and Table II).

It has been reported that upon irradiation with conventional light sources *p*-benzoquinone does not form Paterno–Büchi adducts with styrene.[15] However, upon irradiation with an argon laser source, Paterno–Büchi adducts can be isolated, albeit in low yields (Scheme III and Table II). These adducts consist of the oxetane **4** and the dihydrobenzofuran **6**. This latter substance apparently arises from the oxetane **5** via a very facile dienone–phenol rearrangement. Both the amount of the *p*-benzoquinone consumed and the amount of the products formed are very sensitive to the oxygen concentration (Table II). At an oxygen pressure of 12 atm most of the quinone is consumed and converted in high yield to the trioxane **1b**. Since **1b** has incorporated a molecule of oxygen, its enhanced yield at high oxygen pressures is not surprising. What is surprising is that at low pressures of oxygen the yields of the Paterno–Büchi adducts **4** and **6** are enhanced also, even though these products do not incorporate oxygen during their formation. Subsequent to the observation of this phenomenon,[16] several groups have reported a similar effect of oxygen and other paramagnetic species.[2i,k] These workers have attributed this yield-enhancement effect to the interaction between the paramagnetic species and a triplet biradical intermediate. The paramagnetic species apparently catalyzes the spin inversion of the triplet biradical to the singlet biradical that may either fragment to the starting materials or close to the cycloadduct, in this case the oxetane. Apparently, the ratio of oxetane formation to fragmentation back to starting material is higher in the oxygen-catalyzed process than in the spontaneous process.

The formation of these products is outlined in Scheme IV. The portion of Scheme IV enclosed by the black box is an area of mechanistic uncertainty. It has been traditional to represent the Paterno–Büchi reaction as proceeding through a preoxetane biradical, but in fact very little is known about the intermediates

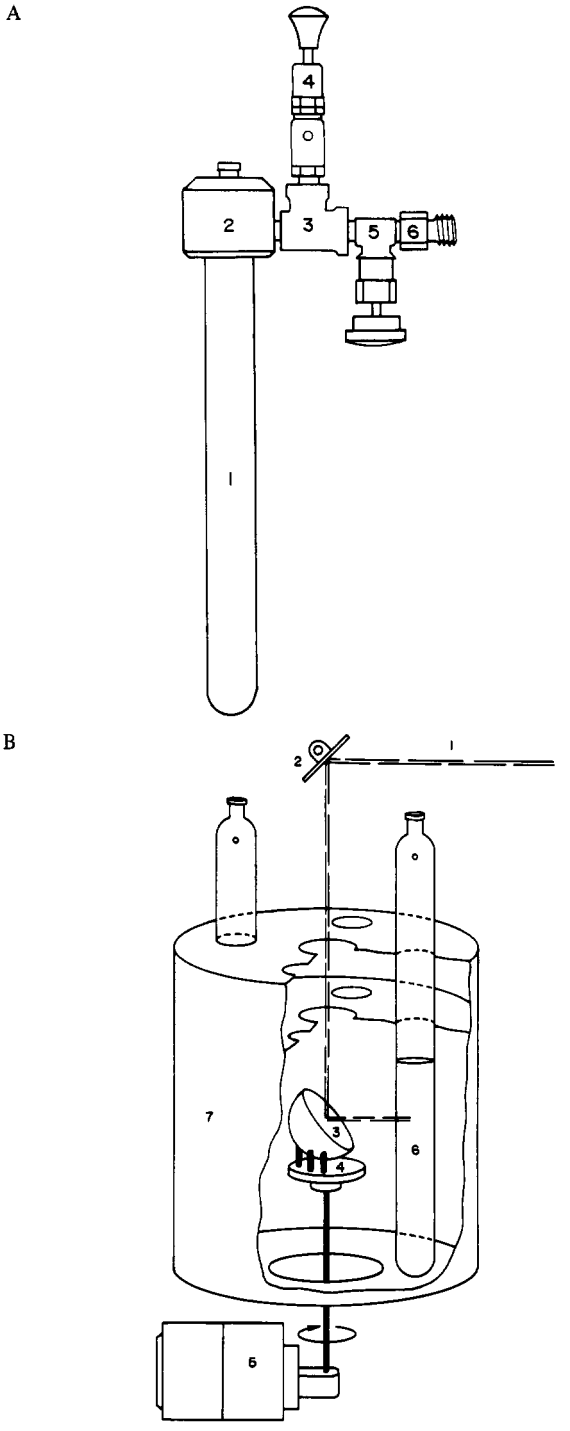


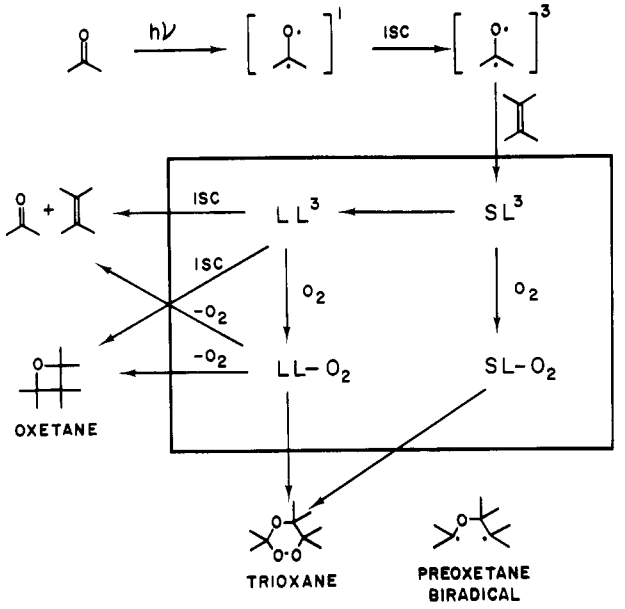
Figure 1. (A, top) Griffin–Worden tube irradiation vessel with pressure fittings: (1) borosilicate or quartz tube (Kontes); (2) endcap with gasket (Kontes); (3) street tee, $^1/_8$ in. NPT (Cajon); (4) safety pressure relief valve, $^1/_8$ in. inner NPT, adjustable from 100 to 200 psi (Nupro); (5) shut-off valve, straight pattern, regular stem, $^1/_8$ in. inner NPT inlet and outlet (Whitey); (6) connector, outer $^1/_8$ in. NPT to inner $^1/_4$ in. tube (Swagelok). (B, bottom) Lighthouse photochemical reactor: (1) argon laser beam; (2) front-surface mirror; (3) front-surface mirror; (4) magnetic mirror mount; (5) drive motor; (6) Griffin–Worden tube without endcaps and connections; (7) stainless steel irradiation chamber.

that may occur in this black box. The oxygen-pressure studies described above and in the remainder of this section serve as a very useful technique for probing the nature of these intermediates. Apparently there are two ways that oxygen can affect the Paterno–Büchi reaction. There is a *direct oxygen effect* in which the products that incorporate oxygen, the trioxanes, increase with increasing oxygen pressure. Also, there is an *indirect oxygen effect* in which the products that do not incorporate oxygen, the oxetanes

(15) Bryce-Smith, D.; Gilbert, A.; Johnson, M. G. *J. Chem. Soc. C* **1967**, 383.

(16) Wunderly, S. W., Ph.D. Dissertation, University of Cincinnati, 1974.

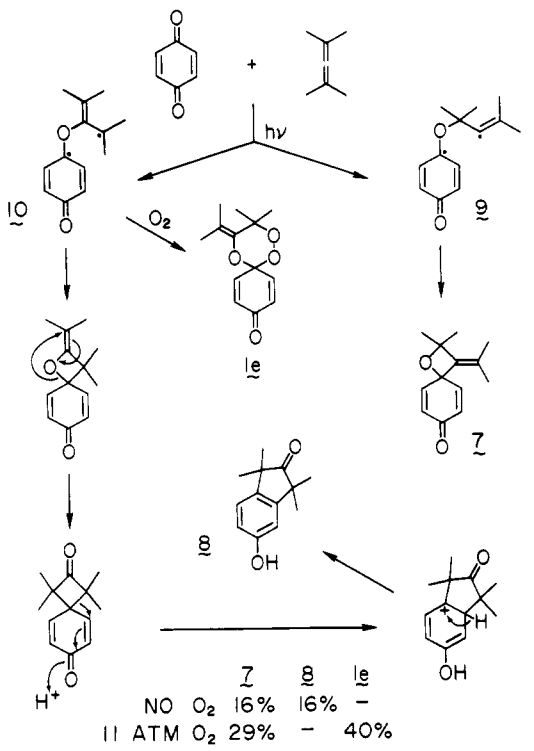
Scheme IV



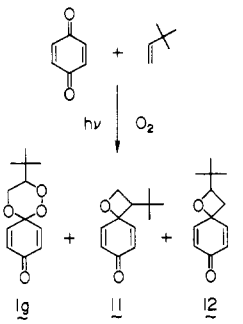
and their rearrangement products, increase with increasing oxygen pressure. However, the indirect oxygen effect is apparent only at low oxygen pressures. At high oxygen pressures the trioxane is essentially the only product formed. The fact that trioxane formation can completely dominate the reaction at high oxygen pressures indicates that the product distribution is not determined solely by the spin statistics of the triplet–triplet, oxygen–preoxetane biradical collision complex.[2i,k] Instead, these products must arise from the interaction of oxygen with at least two different intermediates that occur in our black box (Scheme IV), an initially formed short-lived intermediate (SL) that can be trapped at high oxygen pressures and that apparently affords only trioxane and a subsequently formed long-lived intermediate (LL) that can be trapped at low oxygen pressures and that affords oxetanes and possibly trioxane as well. This is not the behavior expected for preoxetane biradicals. In this traditional picture the long-lived triplet preoxetane biradical would be formed initially and subsequently undergo intersystem crossing to the short-lived singlet preoxetane biradical. If this were the case, the effect of increasing oxygen pressure would be to increase the trapping efficiency of the triplet biradical, and the influence of the singlet biradical would be minimal; the ratio of oxetane to trioxane should remain more or less constant. For this reason it would seem that the singlet preoxetane biradical plays no active role in this trapping reaction.[17] The nature of the two intermediates formed in the styrene system cannot be established from these results alone. However, it seems likely that the long-lived intermediate (LL) is the triplet preoxetane biradical.

In the above styrene example, as well as most other unsymmetrical olefins studied, a single trioxane is formed and this trioxane is apparently derived from trapping of the more stable of the two possible biradical regioisomers. The reaction of *p*-benzoquinone with tetramethylallene provides the most striking example of this regiospecificity. Irradiation of *p*-benzoquinone in the presence of tetramethylallene under anaerobic conditions affords two products, **7** and **8** (Scheme V).[18] The oxetane **7** apparently arises from the less stable vinyl biradical **9**, whereas the benzocyclopentenone **8** can be rationalized as arising from the more stable allyl biradical **10** via the sequence of rearrangements outlined in Scheme V. If this is true, then **10** might be the longer lived of the two intermediates, **9** and **10**, and it might be possible to trap **10** selectively. Indeed, this expectation is realized when the irradiation is conducted under 11 atm of oxygen. Under these conditions, the formation of the allyl biradical product, the cyclopentenone **8**, is suppressed and the trioxane **1e** is formed in its place. On the other hand, the yield of the vinyl biradical product, the oxetane **7**, is unaffected or perhaps slightly enhanced by the presence of oxygen. These results are in complete accord with the existence of two mutually exclusive reaction pathways, one of which proceeds through a relatively long-lived allyl biradical intermediate and the other through a vinyl biradical that is too short-lived to be trapped by oxygen.[19]

Scheme V



Scheme VI



In a similar type of experiment, the effect of oxygen pressure upon the ratio of oxetanes **11** and **12** produced in the irradiation of *p*-benzoquinone and *tert*-butylethylene (Scheme VI) was examined. When this reaction was conducted under anaerobic conditions, the ratio of oxetanes **12**:**11** was determined to be 1.0:3.0 by NMR. Reactions conducted under increasing pressures of oxygen lead to the formation of a single trioxane **1g**. This trioxane again appears to result from the oxygen trapping of the more stable biradical, the same biradical that gives rise to the oxetane **11**. Here

(17) The singlet preoxetane biradical probably occurs between the triplet species and products, but is to short-lived to be trapped. In other oxygen-trapping studies with biradicals derived from azoalkanes, it has never been possible to trap singlet biradicals (ref 2m,o).

(18) (a) Tetramethylallene–benzoquinone: Ishibe, N.; Tanigushi, I. *Tetrahedron* **1971**, *27*, 4883. (b) Other allene–carbonyl systems: Arnold, D. A.; Glick, A. H. *Chem. Commun.* **1966**, 813. Gotthardt, H.; Steinmetz, R.; Hammond, G. S. *Ibid.* **1967**, 480. *J. Org. Chem.* **1968**, *33*, 2774.

(19) It is conceivable that the vinyl biradical is trapped too and that the resulting vinyl peroxide is too unstable to isolate. If this does occur, it cannot be a major reaction pathway since we have never detected vinyl peroxide decomposition products and since the yield of oxetane 7 is not reduced by the trapping of its precursor biradical.

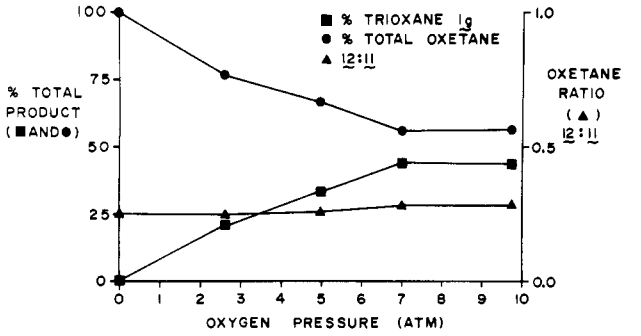


Figure 2. The yields of trioxane **1g** and oxetanes **11** and **12**, and the ratio of oxetanes **12**:**11** as a function of oxygen pressure.

again, we have what appears to be the same situation that we had in the tetramethylallene case. The more stable biradical, that which leads to oxetane **11**, is longer-lived and trapped by oxygen, but the less stable biradical, that which leads to oxetane **12**, is too short-lived to be trapped by oxygen. If this is the case, then increasing oxygen pressure should enhance the efficiency of the biradical trapping and selectively remove the preoxetane–**11** biradical, increasing the oxetane ratio **12**:**11**. A careful study of the oxygen pressure dependence of the oxetane ratio (Figure 2) led to the surprising result that this oxetane ratio is independent of oxygen pressure.

This unexpected result might be interpreted in either of two ways. (1) An initial quinone–olefin intermediate is not involved in trioxane formation. (2) The preoxetane–**11** biradical is not the species being trapped, but instead a prior quinone–olefin intermediate, which has not yet undergone conversion to the two preoxetane biradical regioisomers, is the species being trapped. Such an intermediate might be related to the short-lived intermediate observed in the styrene system (SL in Scheme IV).

If quinone–olefin intermediates are not involved in trioxane formation, then the relevant interaction must be between the excited benzoquinone and molecular oxygen. Such an interaction might result in the formation of either singlet oxygen or a quinone–oxygen adduct (vide infra, Scheme XIX). In order to evaluate this possibility, it was necessary to obtain a measure of the relative reactivity of the triplet n,π^* quinone with olefins and with oxygen. In order to do this in the least equivocal manner, it was further necessary to find a quinone–olefin system that does not produce intermediates that can interact with oxygen. Fortunately, benzoquinone does undergo a high-yield photoaddition to acetylenes to form quinone methides,[20] and these systems do not produce intermediates that are trapped by oxygen at pressures below 15 atm. Furthermore, diphenylacetylene (DPA, Scheme VII) affords a quinone methide (QM, Scheme VII) that is ideally suited for spectroscopic quantum yield determinations, since it exhibits an intense absorption maximum at 337 nm (ϵ = 19 700). Thus, the quenching of benzoquinone triplets by oxygen and olefins can be monitored by following QM formation as outlined in Scheme VII. In the presence of oxygen, the Stern–Volmer expression for QM formation is eq 1. In the absence of oxygen but in the presence of styrene at the same DPA concentration, the Stern–Volmer expression for QM formation becomes eq 2. In this latter case, it is assumed that oxetane formation is negligible. The ratio of the slopes of these two plots should provide the desired measure of triplet quinone reactivity toward styrene and oxygen. These experiments have been conducted by using the regulated output of the 514-nm laser line (see Experimental Section), and the results are presented in Figure 3. These results clearly demonstrate that triplet benzoquinone is quenched at a significantly higher rate by styrene than by oxygen, k_{qs}/k_{qo} = 5.93. Statistically meaningful data sets have not been acquired for other olefins. However, limited quenching studies with nonconjugated olefins such as *tert*-butylethylene indicate that they have triplet

(20) Zimmerman, H. E.; Craft, L. *Tetrahedron Lett.* **1964**, 2131. Bryce-Smith, D.; Fray, G. I.; Gilbert, A. *Ibid.* **1964**, 2137.

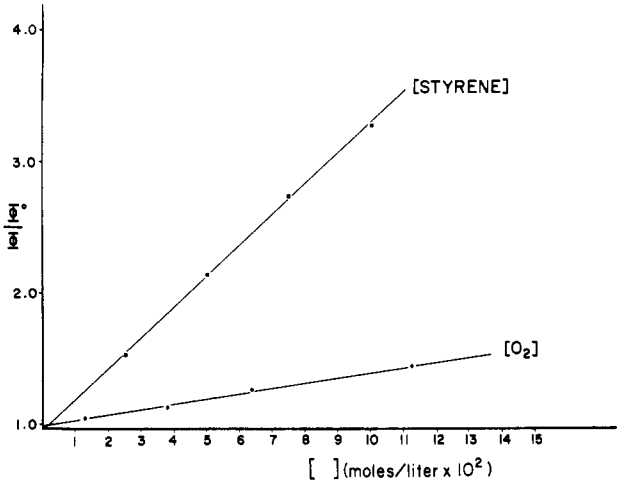
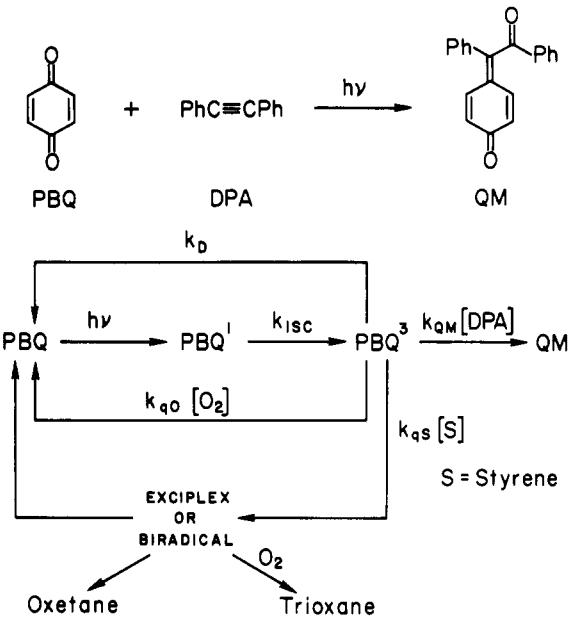


Figure 3. Stern–Volmer relationships for the quenching of triplet benzoquinone:by oxygen, intercept = 0.986, slope = 3.96; r = 0.9976; by styrene, intercept = 0.965, slope = 23.49, r = 0.9994; k_{qs}/k_{qo} = 5.93.

Scheme VII



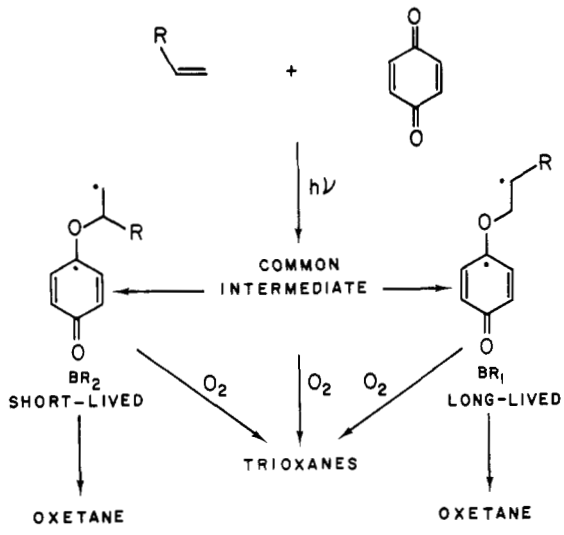
$$\left(\frac{\Phi^\circ}{\Phi}\right)_{QM-O_2} = 1 + \frac{k_{qo}[O_2]}{k_D + k_{QM}[DPA]} \qquad \text{Eqn. 1}$$

$$\left(\frac{\Phi^\circ}{\Phi}\right)_{QM-S} = 1 + \frac{k_{qs}[S]}{k_D + k_{QM}[DPA]} \qquad \text{Eqn. 2}$$

benzoquinone quenching rate constants intermediate between those of styrene and oxygen. While these results do not exclude the possibility that quinone–oxygen interactions are involved in trioxane formation, they do indicate that quinone–olefin intermediates are formed more readily and, therefore, are probably the intermediates that lead to trioxanes.

To return to the *tert*-butylethylene case, it would seem that the only explanation for the invariance of the oxetane ratio with oxygen concentration is that oxygen is trapping an intermediate which occurs before partitioning into the biradicals. This also requires that the preoxetane–**11** biradical is not trapped by oxygen to a significant extent. It is interesting that *trans*-di-*tert*-butylethylene smoothly forms an oxetane with benzoquinone, but no trioxane is formed even under high oxygen pressure. Apparently, the

Scheme VIII



stability of the intermediate that is being trapped, or the trapping process itself, is very sensitive to steric factors.

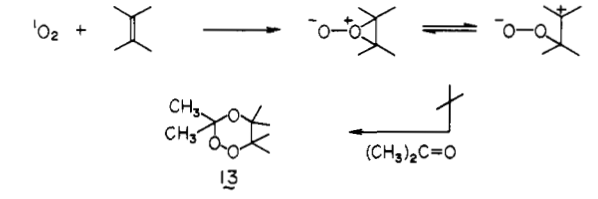
Scheme VIII summarizes the possible trapping processes that might occur with an unsymmetrical olefin. In general, unsymmetrical olefins should give rise to two biradicals. The only case in which we have been able to realize the trapping of both of these biradicals is with vinyl acetate (olefin 10, Table I). In all other cases of unsymmetrical olefins, the trioxanes formed are those that are formally derived from the more stable biradicals (BR_1, Scheme VIII). However, preoxetane biradical trapping appears to occur only when the olefin-derived terminus is highly delocalized as with tetramethylallene and possibly styrene. When the olefin-derived terminus is a simple primary or secondary center as with *tert*-butylethylene, the preoxetane biradical appears too short-lived to be trapped, and only a prior intermediate is trapped. In fact this type of initially formed intermediate may play a more general role in trioxane formation than preoxetane biradicals, since styrene seems to form a similar trappable intermediate. Finally, when the preoxetane biradical contains an sp^2 olefin derived terminus as with allenes and acetylenes, no trappable intermediates are formed. Other than these somewhat crude correlations, very little is known about the structural factors that influence preoxetane biradical lifetime and reactivity. On the other hand, substantially more information is available regarding the nature of the initially formed intermediate, and this will be presented in a later section.

Effect of Temperature. The yield of trioxane formation often is improved significantly by conducting the irradiations at low temperatures. The magnitude of this effect can be substantial, as indicated for olefin 13 in Table I. As a result of this observation, we now routinely conduct all irradiations in a high-pressure, Griffin–Worden tube that is jacketed with an aluminum heat sink through which methanol is circulated at temperatures as low as −30 °C. The explanation for this yield enhancement is not certain. It may be due to the greater solubility of oxygen or to the increased lifetimes of the intermediates that are being trapped in the cold solutions.

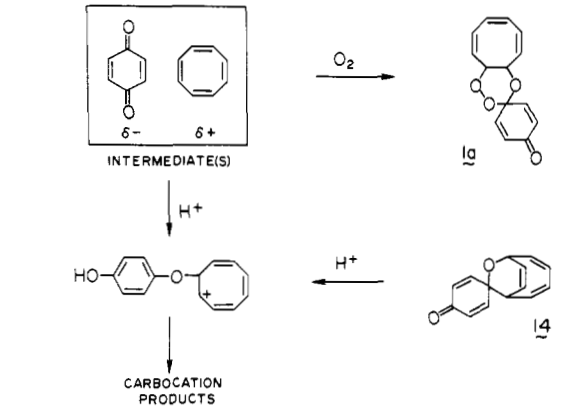
Effect of Solvent. Trioxane formation proceeds well in most solvents such as Freon-11 ($CFCl_3$), carbon tetrachloride, methanol, acetone, and others. The fact that acetone-derived trioxanes (**13**)[21] are not formed when the irradiations are conducted with acetone as solvent (Scheme IX) is one of the lines of evidence that strongly suggests that singlet oxygen is not involved in trioxane formation.[2d,g]

A very intriguing observation was made early in this work. When acetic acid was used as the solvent in the *p*-benzoquinone–cyclooctatetraene reaction (Table I), the yield of trioxane **1a** dropped from its usual value of about 49% in a variety of other solvents to 0%. Furthermore, the products isolated[2d] implied that the intermediate that is usually trapped by oxygen had been protonated by the acetic acid (Scheme X) and undergone carbocation reactions that are usually associated with the acid-catalyzed decomposition of the normal Paterno–Büchi adduct **14**. Subsequent work with other olefins has shown that this phenomenon is general.[22] For example, trioxane formation from 1,1-dicyclopropylethylene also is completely quenched by acetic acid, and carbocation products are formed in its place. On the other hand, norbornene forms a trioxane that is not completely quenched by acetic acid and that forms in direct competition with carbocation rearrangement products.[22] This carbocation mode of reaction is not a simple function of the polarity of the medium, since it is not generally observed with solvents that are significantly more polar than acetic acid, such as methanol or aqueous acetone. Furthermore, it is observed most frequently with olefins that can afford unusually stable carbocations and is not a simple function of the olefin ionization potential. These observations indicate that the quinone–olefin intermediate that is being trapped by oxygen has polar character and, in those systems where a particularly stable carbocation is available, may be protonated before it can be trapped by oxygen. The polarity of the medium may alter to some extent the nature of this intermediate, but not so drastically as to prevent reaction with oxygen provided this occurs prior to an irreversible protonation step. The polar nature of this intermediate does not seem to be consistent with a simple preoxetane biradical of the type shown in Scheme IV. However, it is consistent with a quinone–olefin, charge-transfer (C-T) complex, an exciplex. The possibility that the aforementioned initial intermediates encountered in the styrene and *tert*-butylethylene systems are analogous CT complexes will be developed further in a later section.

Scheme IX



Scheme X



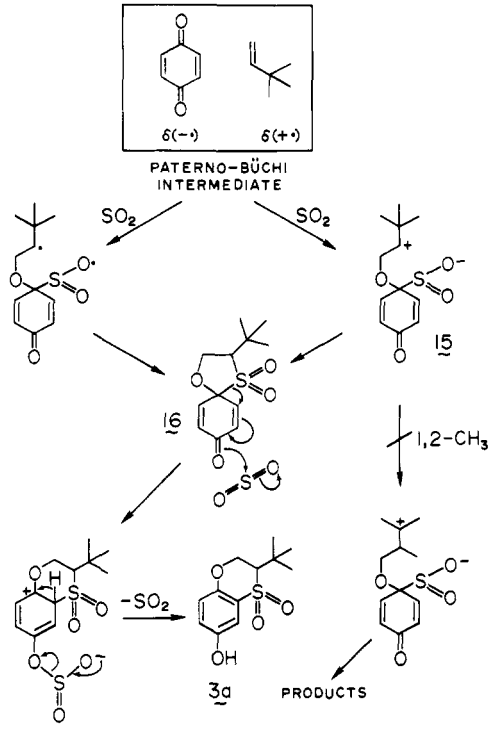
Synthesis of Sulfones

Another reagent that seems to function as an effective trapping agent for photochemical intermediates, including those involved in the Paterno–Büchi reaction, is sulfur dioxide (Schemes II and XI).[6] The advantage of trapping with sulfur dioxide instead of

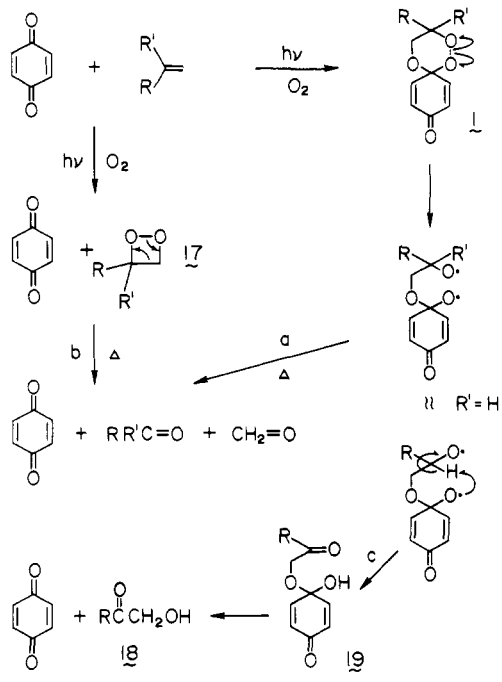
(21) Payne, G. B.; Smith, C. W. *J. Org. Chem.* **1957**, *22*, 1682. Schulz, M. *Adv. Heterocycl. Chem.* **1967**, *8*, 182. Adam, W.; Rios, A. *J. Chem. Soc. D* **1971**, 822.

(22) Wilson, R. M.; Musser, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1720. This paper relates our initial results dealing with the interaction of acids and nucleophiles with quinone exciplexes. Further results in this area will be presented in the near future.

Scheme XI



Scheme XII



oxygen is that high-pressure equipment is not necessary in order to achieve high concentrations of the trapping agent in solution (see Experimental Section). The principal disadvantage of sulfur dioxide is that it does not seem to have as wide a scope as oxygen. Thus, sulfur dioxide yielded no isolable trapping products in the *p*-benzoquinone–cyclooctatetraene system. However, *p*-benzoquinone with cyclohexene, *tert*-butylethylene, and vinyl acetate all formed sulfones with sulfur dioxide (**3** in Scheme II and Table I).

The regiospecificity of these sulfur dioxide trapping reactions parallels that of the oxygen trapping reactions. Of all the olefins investigated in the oxygen trapping experiments, only vinyl acetate provided firm evidence for the formation of the two possible isomeric trioxanes, **1l** and **1m**. In a much more limited series of olefins, sulfur dioxide forms a single sulfone **3a** with *tert*-butylethylene and two sulfones, **3c** and **3d**, with vinyl acetate. These results imply that both oxygen and sulfur dioxide are trapping the same Paterno–Büchi carbonyl–olefin intermediate(s).

Because of the relatively high concentrations of sulfur dioxide employed, it seems likely that the initial Paterno–Büchi intermediate, which has both biradical and dipolar character, is the species being trapped. Since sulfur dioxide can function as a radical trap[23] or as a Lewis acid,[24] it might trap the Paterno–Büchi intermediate via a radical mechanism, as does oxygen, or via an ionic mechanism, as does acetic acid. If the ionic mechanism was involved, one would expect the neopentyl carbocation **15** (Scheme XI) to be on the reaction pathway. The fact that no methyl migration from this carbocation is observed would seem to exclude this ionic pathway. The sequence of events involved in this trapping reaction is uncertain. The sulfur dioxide could react initially with the olefin- or quinone-derived terminus. In the former case, a thermodynamically more stable dienone biradical would result. However, the latter alternative might be kinetically more favorable due to the steric hindrance of the *tert*-butyl group and the radical-anion character of the quinone-derived moiety, which should facilitate attack by Lewis acids such as sulfur dioxide. Scheme XI outlines this latter route. However, either pathway would be expected to result in the spirosulfone **16**. Repeated attempts to isolate or to detect spirosulfone **16** and related intermediates have failed. These spirosulfones would be expected to be very labile toward rearrangement to the stable phenolic sulfones, **3a**, which are the sole products of these reactions. These reactions are conducted in the presence of a large excess of sulfur dioxide that could serve as a Lewis acid to catalyze the dienone–phenol rearrangement from **16** to **3a**. Similar dienone–phenol rearrangements have often been observed under conditions where no more than trace amounts of acid were present.[25]

Trioxane Decomposition. In most cases, the trioxanes (**1**) described here are quite stable substances when pure and in crystalline form. However, in solution they are destroyed slowly by heat or much more rapidly by certain electron-donating ions and by ultraviolet light.

Thermal Decomposition. Two modes of thermal decomposition have been observed. The mode that occurs depends upon the reaction conditions and upon the nature of the substituents at the 6 position of the trioxane ring. If the decomposition is conducted at elevated temperatures either in the gas phase or in solution, all trioxanes, regardless of the substitution at the 6-position, undergo a six-centered fragmentation to afford three carbonyl groups (Scheme XII, pathway a).[2e,g,26] With trioxanes of general structure **1**, these carbonyl constituents consist of the regenerated quinone and the two carbonyl compounds that would have been produced by the singlet oxygen cleavage of the original olefin (Scheme XII, pathway b). Thus, if the intermediate trioxanes could not be isolated, the distinction between the trioxane **1** and the dioxetane **17** pathways for olefin oxidation might be rather tenuous. It seems entirely possible that some carbonyl-sensitized olefin photooxidations might proceed through highly unstable trioxane intermediates rather than through the more conventional dioxetanes (vide infra).

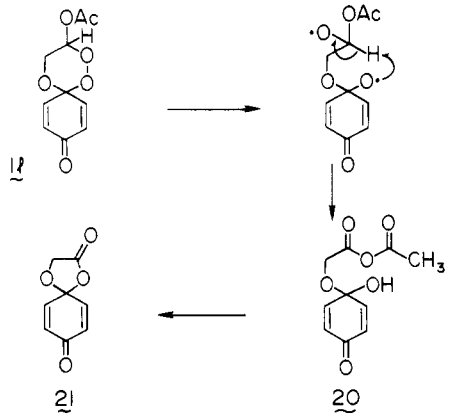
(23) Good, A.; Thynne, J. C. *J. Trans. Faraday Soc.* **1967**, *63*, 2708, 2720. Dainton, F. S.; Ivin, K. J. *Proc. R. Soc. London, Ser. A* **1952**, *212*, 96, 207. Badcock, C. C.; Sidebottom, H. W.; Calvert, J. G.; Reinhardt, G. W.; Damon, E. K. *J. Am. Chem. Soc.* **1971**, *93*, 3115. Sidebottom, H. W.; Badcock, C. C.; Calvert, J. G.; Rabe, B. R.; Damon, E. K. *Ibid.* **1971**, *93*, 3121.

(24) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1951**, *73*, 4169. Grundnes, J.; Christian, S. D.; Cheam, V.; Farnham, S. B. *Ibid.* **1971**, *93*, 20. Rogic, M. M.; Vitrone, J. *Ibid.* **1972**, *94*, 8642.

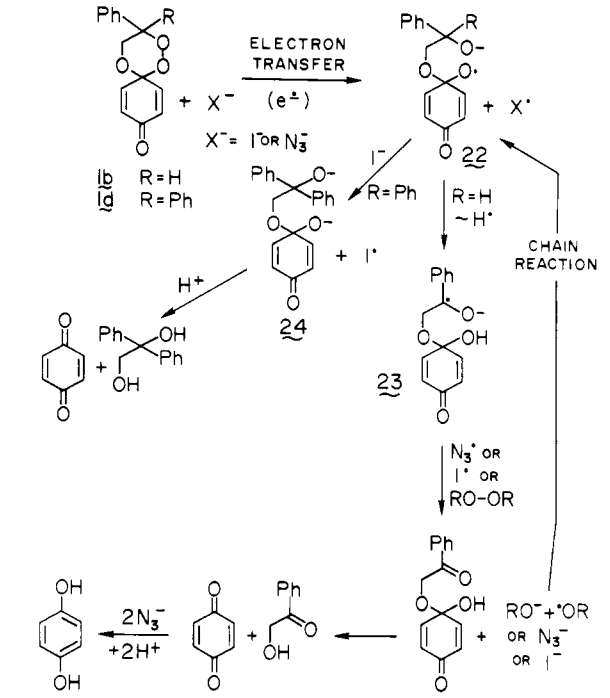
(25) For examples of extremely facile dienone–phenol rearrangements in which acid is not present in more than trace amounts and in which the dienone cannot be detected, see the photoaddition of *p*-benzoquinone to styrene and to tetramethylallene in the Experimental Section.

(26) (a) Schuster, G. B.; Bryant, L. A. *J. Org. Chem.* **1978**, *43*, 521. (b) McCapra, F.; Chang, Y. C.; Burford, A. *J. Chem. Soc., Chem. Commun.* **1976**, 608. (c) Goto, T.; Nakamura, H. *Tetrahedron Lett.* **1976**, 4627. (d) Wasserman, H. H.; Lipshutz, B. H. *Ibid.* **1975**, 4611. (e) Maulding, D. R.; Roberts, B. G. *J. Org. Chem.* **1972**, *37*, 1458.

Scheme XIII



Scheme XIV

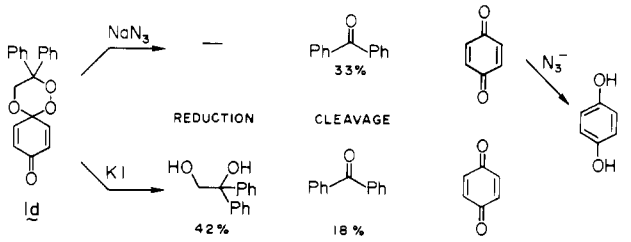


In addition to the six-centered fragmentation process described above, trioxanes may also undergo a six-centered hydrogen abstraction (Scheme XII, pathway c).[2g,26] This process requires that a hydrogen atom be available for abstraction on the 6-position of the trioxane ring and generally occurs at a lower temperature than the six-centered fragmentation. The products of this pathway are the α-hydroxy ketone **18** and the regenerated quinone. It is assumed that the hemiketal **19** is an intermediate in this decomposition. A particularly interesting version of this hydrogen abstraction route is the ambient temperature decomposition of trioxane **1l** (Scheme XIII). In this case, hydrogen abstraction leads to the hemiketal anhydride **20**, which then undergoes an intramolecular acylation to produce the ketal **21**.[27] The reason for the extreme thermal lability of this particular trioxane is not known.

Decomposition Promoted by Electron-Donating Ions. The effect of electron-donating ions upon trioxane decomposition is quite interesting. Anions of this type were investigated initially as possible reagents for the reduction of the trioxane ring system. For years iodide ion has been known to reduce peroxides, and azide ion also has been observed to reduce certain hydroperoxides.[28] When the trioxanes under discussion here are treated with either iodide or azide ion, the major products frequently do not arise from reduction but from greatly accelerated thermal fragmentations related to those discussed in the previous section. Thus, when the 6-phenyltrioxane **1b** is treated with iodide ion, it is cleaved to α-hydroxyacetophenone (33% in 77 h) and *p*-benzoquinone (Scheme XII, pathway c, and Scheme XIV). Azide ion effects the same transformation to α-hydroxyacetophenone in a much shorter time and in appreciably higher yield (68% in 30 min). Similarly, the 6,6-diphenyltrioxane **1d** fragments to benzophenone with either iodide or azide ion, and again azide ion is more effective (Scheme XV). These anions also participate in reduction processes. Azide ion reduces the *p*-benzoquinone formed in the fragmentation to hydroquinone, and peroxide reduction products are formed with iodide ion but not with azide ion (Schemes XIV and XV).[16]

It is interesting to examine these anion-initiated trioxane cleavages within the framework of the chemically initiated electron-exchange luminescence (CIEEL) mechanism for peroxide decomposition that has been proposed recently by Schuster.[29] In this mechanism, the decomposition of peroxides is initiated by an electron transfer from a readily oxidizable aromatic hydrocarbon or amine. This process becomes more effective the greater the electron-donating capacity of the initiator. From this simple criterion, it would seem that the anions studied here should be much better electron donors than the aromatic molecules studied by Schuster. The most effective donor previously studied, rubrene, has an E_{oxidn} = 0.82 eV (CH_2Cl_2) vs. SCE. This compares with iodide ion, which has E_{oxidn} = 0.36 eV (acetone) or 0.37 eV (H_2O) vs. SCE,[30] and azide ion, which has E_{oxidn} = 0.25 eV (H_2O) vs. SCE.[31]

Scheme XV



The trioxane decomposition mechanism suggested in Scheme XIV closely parallels the CIEEL mechanism. Peroxide cleavage could be initiated by electron transfer from the anion. The resulting radical-anion **22** might undergo intramolecular hydrogen transfer to form the ketyl **23**. Ketyl **23** could in turn donate an electron to an iodine atom or an azide radical or perhaps more likely to another peroxide molecule. This latter electron transfer would propagate a radical-chain process that would lead to little if any accumulation of reduction products. Alternatively, when hydrogen transfer is not possible, **22**, R = Ph, a second reduction step might take place to form the dianion **24**, which is the precursor to the observed reduction products. Why iodide ion is more effective as a reducing agent and azide ion as a fragmentation initiator will require further and more quantitative studies.

Photochemical Decomposition. All of the trioxanes examined to date have been found to be extremely sensitive to ultraviolet light. Unfortunately, the product mixtures that result from these photodecompositions are very complex. Consequently, we have only examined one such reaction in detail.

For years, the photooxidation of the menaquinones has been recognized as a means of interrupting electron transport in mi-

(27) Meyers, M. B.; Gallagher, M. J.; Orr, F. F. *Proc. R. Ir. Acad., Sect. B* **1977**, *77B*, 507. Brown, A. E.; Carson, J. A. W.; Gallagher, M. J.; Meyers, M. B. *Spec. Pub. Chem. Soc.* **1977**, *No. 29*, 122.

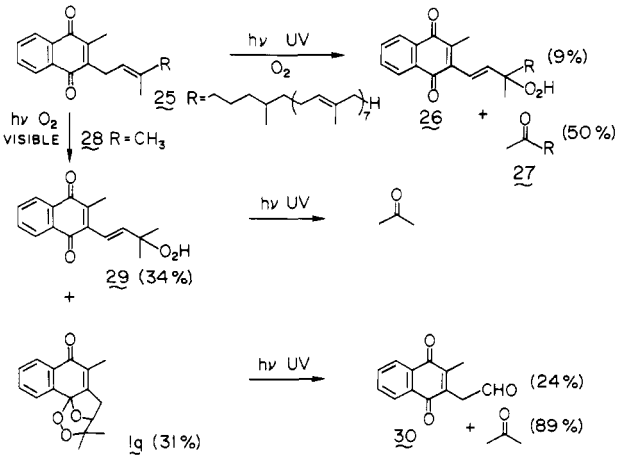
(28) Gollnick, K.; Haisch, D.; Schade, G. *J. Am. Chem. Soc.* **1972**, *94*, 1747.

(29) Schmidt, S. P.; Schuster, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 1966. Koo, J.; Schuster, G. B. *Ibid.* **1978**, *100*, 4496. See also: McCapra, F. *J. Chem. Soc., Chem. Commun.* **1977**, 946.

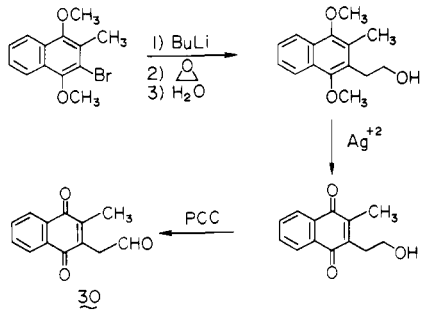
(30) Desideri, P. G.; Lepri, L.; Heimler, D. *Encycl. Electrochem. Elem.* **1973**, *1*, 91.

(31) Lieth, W. J. P. *Encycl. Electrochem. Elem.* **1978**, *8*, 321. Ward, G. A.; Wright, C. M. *J. Electroanal. Chem.* **1964**, *8*, 302. Schafer, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 158.

Scheme XVI



Scheme XVII

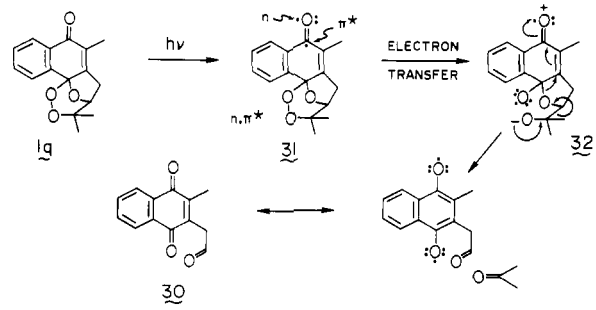


tochondria and other organelles.[32] Snyder and Rapoport have traced this photochemical lability of the menaquinones (vitamin K homologues) to the oxidative cleavage of the prenyl side chain (Scheme XVI).[33] Irradiation of menaquinone-9 (MK-9), **25**, with a 15-W General Electric blacklight under aerobic conditions produced the hydroperoxide **26** as the minor product and the ketone **27**, which resulted from the cleavage of the side chain, as the major product. The fate of the naphthoquinone moiety was never determined. However, Snyder and Rapoport did establish that this oxidation was not a singlet oxygen process but seemed to involve some type of "complex" between the quinone carbonyl, the double bond in the side chain nearest to the quinone nucleus, and oxygen.

We have now reexamined this reaction using menaquinone-1 (MK-1), **28**, since it was suspected that this complex was a trioxane that had been formed and rapidly destroyed by the ultraviolet light source used.[2g,34] This route has now been confirmed. Irradiation of MK-1 (**28**) with the 457.9-nm line of the argon laser under a high-pressure oxygen atmosphere leads to two major products in moderate yields, a hydroperoxide, **29**, analogous to the one found by the previous workers and a trioxane, **1q** (Scheme XVI). The trioxane **1q** was isolated and irradiated with the ultraviolet output of the argon laser (2.8 W at 363.8 and 351.1 nm and several lines around 335 nm). The rapid destruction of **1q** was accompanied by the formation of an equivalent of acetone (89% as determined by NMR and 47% as determined by isolation of a 2,4-DNP derivative). Rapid silica gel chromatography yielded an aldehyde, which was very sensitive to light, and silica gel. The structure of this aldehyde, **30**, was confirmed by comparison with an authentic sample prepared as indicated in Scheme XVII.

The mechanism by which the hydroperoxide **29** is formed is not certain,[35] but it is probably not related to the mechanism of

Scheme XVIII



trioxane formation as suggested in an earlier paper.[34] In this work, the photochemical decomposition of **29** was examined by using the ultraviolet lines of the argon laser. A high yield of acetone (90%) again was observed spectroscopically; however, in this case, none of the aldehyde **30** could be detected. Furthermore, direct chromatographic comparison of **1q** with the reaction mixtures of irradiated **29** at various stages of completion indicated that the trioxane **1q** was not present as an intermediate in this photodecomposition. These observations, plus the fact that no discrete products other than acetone could be isolated from this reaction, provide little information of substance with a bearing on the mechanism of the photodecomposition of hydroperoxide **29**.

In contrast, the photodecomposition study of trioxane **1q** clearly establishes trioxanes as intermediates in the photodecomposition of the menaquinones. Furthermore, it demonstrates that vitamin K trioxanes are quite stable thermally and are formed readily with visible light in the blue–green region of the spectrum, but are destroyed rapidly by ultraviolet light. The products of this photodecomposition are reminiscent of the six-centered thermal fragmentation reaction observed with the aforementioned simple trioxanes. It is interesting to note that electron-transfer processes also might play a role in the photodecomposition of trioxanes. A formal representation of how this might occur is outlined in Scheme XVIII. Thus, excitation of the dienone chromophore to the n,π^* excited state **31** might provide a readily available π^* electron for donation to the peroxide. Electron transfer from the excited carbonyl to the peroxide linkage would result in the charge-separated species **32**, which would be expected to fragment to the quinone aldehyde **30**. Further work dealing with the photosensitized decomposition of peroxides is necessary to evaluate the intriguing possibilities associated with this type of electron transfer.

Oxygen-18 Labeling of Trioxanes. With a knowledge of trioxane chemistry in hand, it has been possible to conduct an oxygen-18 labeling study of trioxane formation.[2e] Such a study was desirable, since it would not only provide information bearing on the possibility of oxygen scrambling in the trioxane formation process but also provide information bearing on the regiospecificity of trioxane formation with respect to the olefin component.

In a control experiment, *p*-benzoquinone was irradiated under an atmosphere of 50% enriched oxygen-18. Under these conditions, no incorporation of oxygen-18 into the quinone carbonyls was observed. Irradiation of *p*-benzoquinone using the same conditions but in the presence of an olefin resulted in oxygen-18 incorporation into the trioxane photoproducts. Several oxygen-18 labeled trioxanes have been prepared in this manner (Table III). These labeled trioxanes have been pyrolyzed in the injection port of a gas chromatograph to yield the three carbonyl components that are characteristic of the six-centered fragmentation process (Scheme XII, pathway a): *p*-benzoquinone, formaldehyde, and RR'CO. The *p*-benzoquinone and RR'CO components were collected, and the extent of oxygen-18 incorporation into these carbonyl compounds was determined by mass spectrometry (Table III).

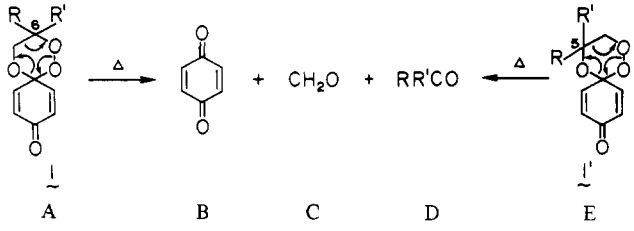
(32) Brodie, A. F. In "Biochemistry of Quinones"; Morton, R. A., Ed.; Academic Press: New York, 1965; p 384. Rounds, D. E.; Olson, R. S. *Z. Zellforsch. Mikrosk. Anat.* **1968**, *87*, 193.

(33) Snyder, C. D.; Rapoport, H. *J. Am. Chem. Soc.* **1969**, *91*, 731.

(34) Wilson, R. M.; Walsh, T. F.; Gee, S. K. *Tetrahedron Lett.* **1980**, 3459.

(35) The hydroperoxide **29** arises from a dark reaction of the photochemically produced quinone methide possibly through a radical chain process: Creed, D.; Werbin, H.; Daniel, T. *Tetrahedron Lett.* **1981**, 2039.

Table III. Theoretical and Observed Oxygen-18 Label Distribution for Trioxane Formation



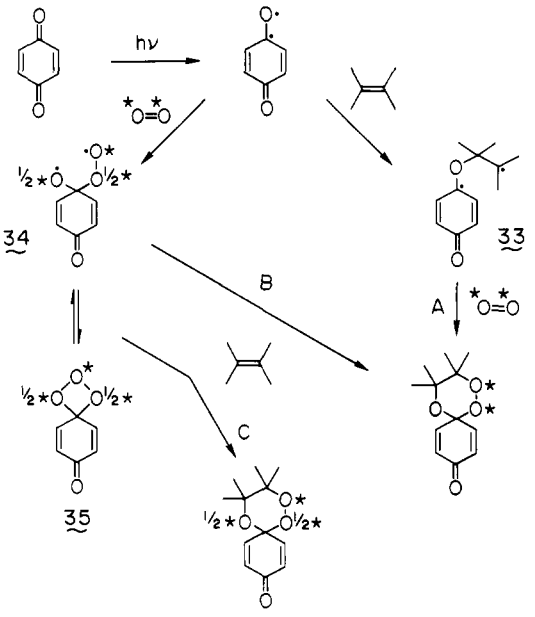
	theoretical label distribution based upon Scheme XIX, %				
pathway	A	B	C	D	E
A	100	50	0	50	
A		50	50	0	100
B	100	50	0	50	
B		50	50	0	100
C	100	25	25	50	
C		25	50	25	100
	observed label distribution, %				
1b, R = Ph R' = H		42		44	
1d, R = Ph R' = Ph		50		52	
1f, R = *t*-Bu R' = H		45		48	

In the interpretation of these labeling data it is important to note that the label distribution depends upon the structure of the trioxane. In those cases where a trioxane is derived from an unsymmetrical olefin, two trioxane isomers are possible, the 6-substituted isomer (**1** in Table III) and the 5-substituted isomer (**1′** in Table III). It is usually not possible to distinguish between these two isomers on the basis of spectroscopic evidence alone. Other methods frequently are necessary in order to make this type of structural assignment; these include X-ray crystallography,[2b,d] sodium borohydride reduction,[2a,34] or chemical degradation (Schemes XIII–XV). In Table III, the theoretical label distributions for both possible trioxane isomers, the 6-substituted isomer **1** and the 5-substituted isomer **1′**, are included as a means of distinguishing between these two regioisomers.

Four mechanisms for oxygen incorporation into the trioxanes have been considered, and three of these are outlined in Scheme XIX.[36] In mechanism A, a quinone–olefin adduct, represented here as a preoxetane biradical (**33**), might be trapped by oxygen to afford a trioxane with the label exclusively in the peroxide linkage. Alternatively, the n,π* excited quinone might form an oxygen adduct initially. If this adduct is the acyclic adduct **34**, again, the resulting trioxane should be labeled exclusively in the peroxide linkage (mechanism B). However, if the adduct is the cyclic trioxetane **35**, the resulting trioxane should be labeled in all trioxane ring-oxygen atoms (mechanism C). The fourth mechanistic possibility involves the formation of singlet oxygen (E_S = 38.5 or 23.5 kcal/mol) by energy transfer from benzoquinone (E_T = 50 kcal/mol). A singlet oxygen–olefin adduct potentially might be trapped by benzoquinone to yield trioxanes. This mechanism is felt to be most unlikely for the following reasons. (1) Excited benzoquinone is quenched at a higher rate by olefins than by oxygen. (2) This rate difference will be greatly enhanced when the quinone and olefin are incorporated into the same molecule as they are in olefins **13** and **14** in Table I. The fact that related electron-deficient olefins, which would not be expected to be good substrates for singlet oxygen, can afford high yields of trioxanes indicates that singlet oxygen is not involved.[2n] Other workers have reached the same conclusions for the naphthoquinone series.[33] (3) If a singlet oxygen–olefin adduct were involved, it might be possible to intercept it with carbonyl compounds other than a quinone. Only the quinone trioxanes are formed when acetone is employed as the solvent even though the acetone trioxanes (Scheme IX) are stable under the reaction conditions. (4) Singlet oxygen products have been observed in this work only in those cases where the olefin has a lower triplet energy than benzoquinone, as, for example, in the case of 1,4-diphenylbutadiene. (5) Silylenol ethers are known to be excellent substrates for singlet oxygen reactions,[37] and yet the characteristic singlet-oxygen products have not been found in this work. Therefore, even though singlet oxygen may be formed in limited quantities under these reaction conditions, it is clear that it plays no role in trioxane formation.

(36) Mechanisms involving singlet oxygen have been excluded as a result of earlier work in these (ref 2d) and other laboratories (ref 33).

Scheme XIX

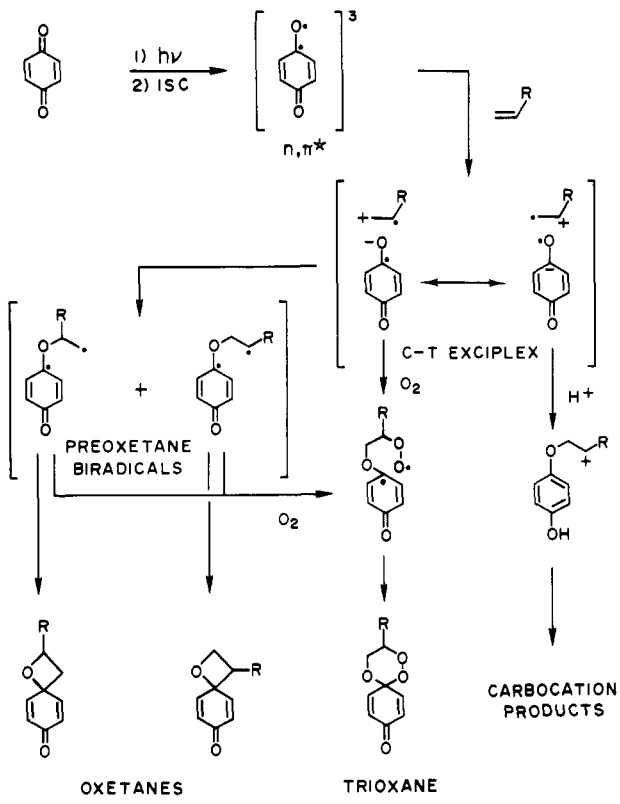


From the above prospective, a comparison of the observed label distributions in Table III with the theoretical label distributions indicates that oxygen is incorporated into the trioxane ring without scrambling by either mechanism A or B and that all of the trioxanes are substituted in the 6-position.

While adducts between oxygen and aliphatic ketones have been invoked as intermediates in the photooxidation of carbonyl compounds,[38] it has been shown that low-energy n,π* triplet carbonyls are not as easily quenched by oxygen as are higher energy n,π* triplet states.[39] This has been attributed to the much smaller charge-transfer contribution, $>C{=}O^{+}\cdots O_2^{-}$, to the stabilization of carbonyl oxygen complexes of low-energy n,π* carbonyl triplets. On the basis of this type of argument, one would expect oxygen quenching or oxygen complex formation with the very low energy triplet n,π* excited state of *p*-benzoquinone to be most inefficient. This correlation is in accord with the previously discussed relative quenching rate studies (Figure 3). Thus, mechanism B in Scheme XIX seems much less likely than mechanism A. In further support of mechanism A are the results of Bartlett and co-workers dealing with the photooxidation of olefins using α-diketones.[40] Here again, oxygen complex formation with the excited states of these carbonyls is not particularly favorable.[39] In an oxygen-18 labeling study done subsequently to that reported here,[2e] Bartlett and Becherer[40c] obtained labeling data that indicated that the excited α-diketone reacts first with the olefin, followed by oxygen trapping of the olefin adduct in much the same fashion as outlined in mechanism A of Scheme XIX. These α-diketone initiated oxidations differ from the quinone oxidations in that polymeric

(37) Jefford, C. W.; Rimbault, C. G. *Tetrahedron Lett.* **1977**, 2375.
(38) Quinkert, G. *Pure Appl. Chem.* **1964**, *9*, 607.
(39) Schuh, M. D. et al. *J. Am. Chem. Soc.* **1980**, *102*, 5656.
(40) (a) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193. (b) Bartlett, P. D.; Landis, M. E. *Ibid.* **1977**, *99*, 3033. (c) Bartlett, P. D.; Becherer, J. *Tetrahedron Lett.* **1978**, 2983.

Scheme XX



peroxides seems to be the intermediates rather than discrete trioxanes.[41]

The Trapping Process

The most straightforward interpretation of the trapping results presented in this paper is that the species being trapped by the oxygen is the triplet preoxetane biradical (Scheme XX). This possibility is consistent with the oxygen trapping results for at least one olefin, tetramethylallene (Scheme V). Furthermore, the oxygen trapping of related biradicals derived from azoalkanes[2m,o] has been demonstrated by using the same laser, high-pressure oxygen technique that is described here. Thus, the preoxetane biradical trapping mechanism is quite reasonable, and probably occurs in some cases.

However, a more detailed examination of these trapping reactions has provided results that cannot be reconciled with this simple interpretation. The results for both styrene and *tert*-butylethylene require that a relevant intermediate precedes the traditional preoxetane biradical and that this intermediate plays a most important role in the trapping process. Competitive trapping with oxygen and acetic acid indicates that this new intermediate is probably a quinone–olefin CT exciplex (Scheme XX). It would be expected that reaction between n,π^* triplet *p*-benzoquinone[42] and olefin would lead to such triplet exciplexes. CNDO calculations predict that formation of triplet quinone–olefin exciplexes should be quite favorable.[21] Duroquinone has been found to form triplet exciplexes with electron-rich aromatics.[43] While duroquinone does not form trioxanes, possibly due to excess steric hindrance, 2,6-dimethyl-*p*-benzoquinone (olefins 2 and 7, Table I) and plastoquinones[2a] form trioxanes in quite respectable yields. Furthermore, the acid quenching of exciplexes arising from the interaction of excited fluoro ketones and substituted benzenes has been observed recently.[44]

It may be that trioxane formation is most facile with electron-deficient carbonyl compounds such as quinones, which should be ideal acceptors in the formation of CT exciplexes with olefins. Perhaps it is significant in this regard that benzophenone also forms trioxanes (olefins 7 and 9, Table I), but these are very inefficient reactions that require long irradiation times in order to obtain very small yields of trioxanes. Also, trioxanes are not formed in intermolecular reactions with electron-deficient olefins. Intramolecular examples of trioxane formation with electron-deficient olefins are known,[2n] but then it is difficult to assess CT contributions in systems such as these where both donor and acceptor are conjugated with each other.

A number of important questions remain to be answered. Both preoxetane biradical and exciplex trapping seem to occur. Where one of these processes completely dominates the trapping, the oxygen pressure dependence of the oxetane ratio can be used to determine which is occurring. However, in systems where both trapping processes may be active, it becomes important to be able to assess quantitatively the contribution of each type of trapping process. How this might be accomplished is not presently known. If the contribution of the preoxetane biradical trapping were known, then this information might be used to gain insight into the steric and electronic factors that influence biradical lifetimes. In addition, very little is known about the sequence of steps involved in oxygen trapping. In order for the trapping to be a concerted process, the collision complex between triplet oxygen and the triplet exciplex or biradical would have to be a singlet. Spin statistics indicate that about one-ninth of such collision complexes would be singlets. On the other hand, about one-third of these complexes should be triplets. Therefore, only about one-fourth of the trapping events could be concerted at maximum; the remaining three-fourths would be stepwise. Oxygen trapping of biradicals derived from azoalkanes leads to products that are best rationalized by a stepwise trapping.[2o] In the quinone–olefin system, the initial trapping might occur at either the olefin or the quinone moiety. Which of these occurs may depend upon whether an exciplex or biradical is the species trapped, and even then electronic and steric factors may cause the site of initial attack to vary from one system to another. In Scheme XX the initial attack has been represented as occurring on the olefin moiety. This sequence is based upon the known trans stereochemistry of the norbornene trioxane **1k** in which the ether oxygen is exo and the peroxide linkage endo. This stereochemistry might be rationalized by an endo attack of molecular oxygen on the olefin moiety of an exo exciplex. However, other explanations are certainly possible. Finally, the trioxane formation is generally a highly regioselective process in contrast to oxetane formation, which is not. This regioselectivity can be rationalized easily for preoxetane biradicals as arising from the selective trapping of the more stable, longer-lived biradical. A satisfactory explanation for the regioselectivity that occurs in exciplex trapping is not presently available, and probably will have to await further information bearing on the exciplex geometry and the trapping sequence.

Summary

The formation of 1,2,4-trioxanes has been shown to be a general reaction that occurs upon irradiation of quinones and benzophenone in the presence of an olefin and oxygen. Application of monochromatic laser light and high oxygen pressures have proved most useful in the study of this unusual photooxidation. Trioxane degradation studies under thermal and photochemical conditions, as well as with iodide and azide ions, have not only aided in the structure determination of the trioxanes but also provided a strong case for the intermediacy of trioxanes in the photodegradation of vitamin K. A mechanistic study of trioxane formation has implicated both quinone–olefin CT exciplexes and preoxetane biradicals as pivotal intermediates in the oxygen-trapping process. The incorporation of these exciplexes, as chemically manipulatable intermediates, into the mechanistic description of quinone–olefin

(41) We have made several attempts to apply our laser techniques to the preparation of trioxanes derived from α-diketones. In none of these instances have we been able to isolate or to obtain spectroscopic evidence for the formation of trioxanes in these reactions. Furthermore, in our extensive studies of trioxane degradation, we have not been able to observe the formation of epoxides in more than trace amounts. The apparent relationship between α-diketone sensitized olefin epoxidation and *p*-benzoquinone or benzophenone trioxane formation is most intriguing, and certainly deserves further attention.

(42) Bruce, J. M. *Q. Rev., Chem. Soc.* **1967**, *21*, 405.

(43) Scheerer, R.; Grätzel, M. *J. Am. Chem. Soc.* **1977**, *99*, 865.

(44) Wagner, P. J.; Thomas, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 4173.

photochemistry not only serves to unify the previously unrelated ionic and radical photoreactions of excited quinones but also provides a rational basis for the further development of new quinone photoreactions.

Experimental Section

General. Melting points are uncorrected and were determined with a Mettler FP-2 hot-stage apparatus with a polarizing microscope. Nuclear magnetic resonance spectra were recorded with Varian Associates T-60 and HA-100 and JEOL FX 90-Q spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane, as an internal standard, and apparent coupling constants (J) are reported in hertz. Infrared spectra were recorded with a Perkin-Elmer Model 337 or 599 spectrophotometer and are reported in reciprocal centimeters (cm^{-1}). Ultraviolet spectra were recorded with a Cary Model 14 spectrophotometer. Mass spectra were determined with a Hitachi RMU-7 spectrometer at an ionizing voltage of 70 eV. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Analytical and preparative thin-layer chromatography was done with EM silica gel 60 F_{254} precoated plates. Column chromatography was done with EM silica gel (less than 0.08 mm). Gas–liquid chromatography was done with a Varian Aerograph Model 90-P instrument. Removal of solvents under reduced pressure was conducted by using a rotary evaporator with a water-aspirator vacuum. Magnesium sulfate was used as a drying agent.

Argon Ion Laser Irradiation Procedures. In the early stages of this work, a Coherent Radiation Model 53A argon ion laser, henceforth referred to as the CR-8 (6–10 W, all lines in the visible region of the spectrum), was used. In more recent work, a Coherent Radiation Model 18 Super Graphite argon ion laser, henceforth referred to as the CR-18 (25–30 W, all lines in the visible, or 3 W, all lines in the ultraviolet), was used. The laser power output was monitored with a Coherent Radiation Model 201 thermal disc power meter. In the experiments described below, the output in all of the visible lines was generally regulated by reducing the laser tube current so as to obtain a total power output of from 2 to 6 W. Where indicated, irradiation with a single visible line was conducted by replacing the rear laser cavity mirror with a prism wavelength selector provided by the manufacturer. In those cases where the ultraviolet output was used, the cavity mirrors coated to reflect the visible lines were replaced with mirrors coated to reflect the ultraviolet lines. The typical output of a new CR-18 laser tube adjusted for maximum gain is as follows: 514.5 nm (9.5 W), 501.7 (1.8), 496.5 (2.8), 488.0 (7.8), 476.5 (3.1), 472.7 (1.4), 465.8 (0.9), 457.9 (1.6), and 454.5 (0.8), for a total of 29.7 W in the visible, or 363.8 nm, 351.4, 351.1, 335.8, 334.5, and 333.6, for a total of 3.3 W in the ultraviolet.

The laser beam was always diverged slightly by passing it through a lens before it was passed into the reaction vessel. The undiverged beam diameter ($1/e^2$ points) was about 1.5 mm depending upon the laser and wavelengths used. This beam was usually expanded to about 5 mm. The reactions discussed here were typically conducted with all of the visible lines from 2 to 7 W. Therefore, for a 4-W beam the approximate light intensities are 5×10^{20} photons cm^{-2} sec^{-1} undiverged and 5×10^{19} photons cm^{-2} sec^{-1} diverged. If the beam is passed directly into the vessel or if it is focused on the reaction vessel wall, pyrolysis at the inner wall of the vessel will occur. The extremely high temperatures developed at this spot where the glass has been blackened can lead to rupture of the vessel or at least to undesirable thermal reactions. The intensity at which this charring occurs depends upon the particular reaction and may be a crude indication of the threshold for multiple photon processes. That multiple photon processes are not involved in the photochemistry studied here is clear, since trioxane formation occurs at much lower light intensities (10^{17-16} photons cm^{-2} sec^{-1}), albeit much more slowly.

For reactions conducted under 1 atm of oxygen, round-bottom flasks were used and oxygen was simply bubbled through the reaction mixtures during irradiation. For reactions conducted under higher oxygen pressures, Griffin–Worden tubes rated at 250 psig (18 atm) were used (see Figure 1A for a detailed description of the tube with attachments). These tubes were fitted with shut-off valves and safety pressure relief valves. The solution to be irradiated was introduced into the tube, the tube pressurized to the desired pressure (~200 psig or ~15 atm), and the solution allowed to equilibrate for ~30 min with periodic shaking before irradiation was begun. All irradiations were conducted at ~4 W with all visible lines unless stated otherwise. During irradiation the tube can be placed in an aluminum cooling jacket, which also serves as an explosion shield. To date no explosions have occurred, although several tubes have ruptured, apparently due to glass fatigue or strain. In this configuration, the laser beam can be introduced through the bottom of the Griffin–Worden tube. If cooling was necessary, cold methanol (−30 °C) was circulated through the cooling jacket with a Haake T-52 circulating bath. Upon completion of the irradiation, the pressure in the tube was released slowly as the solution could effervesce vigorously and spew out of the tube if the pressure was released abruptly.

Irradiation of *p*-Benzoquinone with Styrene. Under Anaerobic Conditions. A solution of 0.962 g (8.90 mmol) of *p*-benzoquinone and 10 mL of styrene in 400 mL of carbon tetrachloride was irradiated with the CR-8 for 10 h with stirring. The reaction mixture was evaporated to dryness and the starting materials separated from the products by rapid chromatography of the residue on a column of 80 g of silica gel eluted with benzene. The products were rechromatographed on three 20 cm × 20 cm thick-layer silica gel plates eluted eight times with benzene. The less polar band was a yellow oil that was tentatively assigned the structure of 7-phenylbicyclo[4.2.0]-3-octene-2,6-dione, 0.297 g (1.4 mmol, 16%); IR (neat) ν_{max} 1665 cm^{-1}; NMR (CCl_4) δ 2.62 (m, 2 H), 3.00–3.95 (m, 3 H), 6.71 (s, 2 H), 7.23 (s, 5 H). The more polar band yielded oxetane **4**, 0.37 g (1.74 mmol, 20%); after recrystallization from ether–pentane: mp 79.2–80.1 °C; IR ($CHCl_3$) ν_{max} 1670, 1640 cm^{-1}; NMR ($CDCl_3$) δ 3.00 (m, 2 H), 5.91 (dd, J = 7 and 7 Hz, 1 H), 6.24 (m, 2 H), 7.1–7.6 (m, 7 H); mass spectrum, m/e 212 (M^+). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 78.95; H, 5.75.

Under 1 Atm of Oxygen. A solution of 1.191 g (11.0 mmol) of *p*-benzoquinone and 9.0 g (86.5 mmol) of styrene in 450 mL of carbon tetrachloride saturated with oxygen and cooled with a cold-finger condenser was irradiated by using the CR-8 for 11 h with rapid stirring. Chromatography on a column of 80 g of silica gel eluted with benzene afforded the trioxane **1b** as a mixture with unreacted *p*-benzoquinone. Recrystallization from methylene chloride–pentane afforded 1.51 g (6.2 mmol, 56%) of **1b**. An analytical sample was obtained by sublimation at 120 °C (0.01 mm) to give colorless crystals: mp 126.2–126.4 °C; IR ($CHCl_3$) ν_{max} 1690, 1640 cm^{-1}; NMR ($CDCl_3$) δ 4.02 (dd, J = 12.0 and 3.5 Hz, 1 H), 4.28 (dd, J = 12.0 and 10.0 Hz, 1 H), 5.46 (dd, J = 10.0 and 3.5 Hz, 1 H), 6.28 (br d, J = 11.0 Hz, 2 H), 6.60 (m, 1 H), 7.33 (br s, 5 H), 7.85 (m, 1 H); mass spectrum, m/e 244 (M^+). Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.82; H, 4.98.

Further elution of the column with benzene afforded a mixture of products as a viscous oil, 0.459 g. Rechromatography of this mixture on silica gel thick-layer plates eluted with benzene yielded, in order of increasing polarity, *p*-benzoquinone; oxetane **4**, 0.203 g (0.96 mmol, 9%); and the dihydrobenzofuran **6**, 0.118 g (0.56 mmol, 5%); after recrystallization from benzene–hexane: mp 66.4–66.7 °C; IR ($CHCl_3$) ν_{max} 3580, 3400, 1600, 1500 cm^{-1}; NMR ($CDCl_3$) δ 4.2–4.9 (m, 3 H), 6.54 (m, 3 H), 7.20 (br s, 5 H); mass spectrum, m/e 212 (M^+). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.02; H, 5.74.

Irradiation in acetonitrile of carbon tetrachloride afforded the trioxane **1b** in only 25% yield.

Under 11 Atm of Oxygen. A solution of 0.234 g (2.16 mmol) of *p*-benzoquinone and 0.681 g (6.54 mmol) of styrene in 40 mL of carbon tetrachloride was placed in a Griffin–Worden tube under 11 atm of oxygen and irradiated by using the CR-8 for ~2.5 h. Under these conditions, the trioxane **1b** was isolated as the only product, 0.4032 g (1.675 mmol, 94% yield based upon the recovery of 0.0432 g of unreacted *p*-benzoquinone).

Apparatus for the Determination of Relative Rate Data by Using a Laser Source (the Lighthouse). This apparatus is illustrated in Figure 1B. It consists of an enclosed stainless steel cylinder with a baffle inside. The two top horizontal members have five holes each that are aligned. The four peripheral holes are for insertion of the sample tubes and are positioned equidistant from the central hole. The central holes in the two top members permit the laser beam to be reflected down into the core of the apparatus. The single large opening in the center of the bottom horizontal member permits the rotating mirror to be introduced into the sample chamber. The rotating mirror is mounted at an angle of 45° by means of a magnetic mount that in turn is attached to the drive shaft of a motor. As the mirror rotates the laser beam is swept through the samples positioned around the mirror.

Relative Rate of the Photoaddition of *p*-Benzoquinone to Styrene as a Function of Oxygen Pressure. A stock solution of 0.934 g (8.64 mmol) of *p*-benzoquinone and 2.72 g (26.1 mmol) of styrene in 160 mL of carbon tetrachloride was prepared. This solution was divided equally between four tubes. One tube was degassed and pressurized (1 atm) with argon, the second tube was pressurized with air (1 atm), the third tube was pressurized with oxygen (1 atm), and the fourth tube was pressurized with oxygen under high pressure (11 atm). The four tubes were placed in the Lighthouse and irradiated with the CR-8 for 8 h. The quantity of unreacted *p*-benzoquinone was determined by ultraviolet absorption spectroscopy at 456 nm, and the yields of photoproducts were determined by isolation as described in the previous sections. The results are recorded in Table II.

Triplet Benzoquinone Quenching Studies. Stock solutions of 0.1 M *p*-benzoquinone (sublimed twice) and 0.1 M diphenylacetylene were prepared in carbon tetrachloride. The Griffin–Worden tubes used in this type of experiment must be carefully selected on the basis of the optical

characteristics of the tube bottom through which the light enters. The tube bottom must have a uniform wall thickness (*no* dimple resulting from the sealing operation) and as large a radius of curvature as possible. A tube that does not have these characteristics will tend to alter the sample volume swept by the beam from run to run such that the optical density standard deviation of the quinone methide determination for a series of runs may be as high as ±0.10, as compared to a selected tube for which these standard deviations are about ±0.01–0.03. A selected Griffin–Worden tube was flushed with either argon or oxygen and 5 mL of each stock solution added. In the oxygen experiments, the tube was pressurized to the desired pressure and allowed to equilibrate for at least 1.5 h with frequent shaking. The time required for equilibrium was established to be ~1 h, as determined by repetitive runs at increasing equilibration times. The tube was mounted in a prealigned and rigid bracket. The CR-18 was put into the light-regulated mode to minimize output power drift between runs (long-term drift ±1%). Each sample was irradiated at 514.5 nm (0.5 W, 4.1×10^{19} photons cm^{-2} sec^{-1}), benzoquinone $\epsilon = 0.6$, for 60 s. Under these conditions conversion was less than 7%. Quinone methide formation was determined by ultraviolet spectroscopy by using the intense quinone methide band at 337 nm (ϵ = 19 700). A pair of short-path (0.252 mm) balanced and calibrated cells were constructed according to the procedure of Heineman and DeAngelis,[45] but with the plastic backing material from EM silica gel 60 F_{254} thin-layer chromatography plates as spacers. These cells were particularly convenient, since they could be used to analyze the concentrated quantum yield runs directly and since Beer's law control studies could be done at these high concentrations. The oxygen concentration was determined from its known solubility in carbon tetrachloride.[46] Similar runs with known amounts of added styrene were conducted under argon. The results from these experiments are summarized in Figure 3, where each point is derived from at least three determinations.

Irradiation of 2,6-Dimethyl-*p*-benzoquinone with Styrene and Oxygen. A solution of 0.18 g (1.32 mmol) of 2,6-dimethyl-*p*-benzoquinone and 1.048 g (10.1 mmol) of styrene in 25 mL of carbon tetrachloride was placed in a Griffin–Worden tube under 12.5 atm of oxygen and irradiated with the 488.0-nm line of the CR-18 (7.7 W) for 0.5 h. Column chromatography on 30 g of silica gel eluted with $CHCl_3$ yielded **1c**. Recrystallization from ether–pentane afforded 0.142 g (0.52 mmol, 40%) of **1c**: mp 110.1–110.7 °C; IR ($CHCl_3$) ν_{max} 1680, 1655 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.92 (d, J = 1.6 Hz, 3 H), 1.98 (d, J = 1.6 Hz, 3 H), 3.92–4.44 (m, 2 H), 5.50 (dd, J = 10 and 4 Hz, 1 H), 6.47 (q, J = 1.6 Hz, 1 H), 7.48 (s, 5 H), 7.62 (q, J = 1.6 Hz, 1 H); mass spectrum, m/e 272 (M^+). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.46; H, 6.04.

Irradiation of *p*-Benzoquinone with 1,1-Diphenylethylene and Oxygen. A solution of 0.336 g (3.12 mmol) of *p*-benzoquinone and 1.352 g (7.51 mmol) of 1,1-diphenylethylene in 200 mL of carbon tetrachloride saturated with oxygen and cooled with a cold finger was irradiated with the CR-8 for 8.25 h with rapid stirring. The excess 1,1-diphenylethylene was removed by rapid column chromatography on 10 g of silica gel eluted with hexane. The column was washed with chloroform. The chloroform fraction residue was rechromatographed on silica gel thick-layer plates eluted with benzene to obtain trioxane **1d** (0.419 g, 1.3 mmol, 42%), benzophenone (0.04 g, 0.21 mmol, 7%), and 3′,3′-diphenylspiro[2,5-cyclohexadiene-1,1′-[2]oxacyclobutan]-4-one (0.03 g, 0.01 mmol, 1%).

After recrystallization from benzene–pentane the trioxane **1d** showed the following: mp 131.4–131.6 °C; IR ($CHCl_3$) ν_{max} 1690, 1640 cm^{-1}; NMR ($CDCl_3$) δ 4.60 (s, 2 H), 6.27 (br d, J = 10 Hz, 2 H), 7.2 (m, 2 H), 7.43 (br s, 10 H); mass spectrum, m/e 320 (M^+). Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 74.96; H, 5.10.

After recrystallization from methylene chloride–pentane the spiro-oxetane showed the following: mp 188.5–189.6 °C; NMR ($CDCl_3$) δ 3.50 (s, 2 H), 6.20 (br d, J = 10 Hz, 2 H), 7.6 (br d, J = 10 Hz, 2 H), 7.40 (m, 10 H); mass spectrum, m/e 288 (M^+). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.36; H, 5.52.

Irradiation of *p*-Benzoquinone with Tetramethylallene. Under 11 Atm of Oxygen. A solution of 0.246 g (2.29 mmol) of *p*-benzoquinone and 0.45 g (4.7 mmol) of tetramethylallene in 35 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 11 atm with oxygen was irradiated with the CR-8 for 0.5 h. The reaction mixture was chromatographed on silica gel thick-layer plates eluted with chloroform–methanol (98:2). The trioxane **1e** was obtained as an oil (0.244 g, 0.91 mmol, 40%). An analytical sample was obtained by distillation at 50 °C (10^{-6} mm): IR (CCl_4) ν_{max} 1685, 1640 cm^{-1}; NMR (CCl_4) δ 1.52 (br s, 6 H), 1.65 (s, 3 H), 1.71 (s, 3 H), 6.22 (d, J = 10 Hz, 2 H), 6.85 (m, 2 H); mass spectrum, m/e 236 (M^+). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.89; H, 6.86.

The oxetane **7** was obtained as a solid (0.135 g, 0.66 mmol, 29%); after recrystallization from pentane: mp 84.1–85.4 °C; IR (CCl_4) ν_{max} 1670, 1640 cm^{-1}; NMR (CCl_4) δ 1.38 (s, 3 H), 1.60 (s, 9 H), 6.13 (d, J = 10 Hz, 2 H), 6.96 (d, J = 10 Hz, 2 H); mass spectrum, m/e 204 (M^+). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.36; H, 7.81.

Under Anaerobic Conditions. A solution of 0.346 g (3.20 mmol) of *p*-benzoquinone and 0.45 g (4.7 mmol) of tetramethylallene in 40 mL of benzene was irradiated by using the CR-8 under argon for 1.0 h. Isolation in the manner described above afforded phenol **8** (0.1049 g, 0.514 mmol, 16%), mp 245–249 °C, with rapid sublimation (lit.[18a] mp 243–244 °C), and oxetane **7** (0.1027 g, 0.503 mmol, 16%).

Irradiation of *p*-Benzoquinone with 1,1-Dicyclopropylethylene and Oxygen. A solution of 0.189 g (1.75 mmol) of *p*-benzoquinone and 0.191 g (1.77 mmol) of 1,1-dicyclopropylethylene in 10 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 13 atm with oxygen and cooled to −10 °C was irradiated with the 488.0-nm line of the CR-18 (7.7 W) for 0.5 h. Chromatography on 10 g of silica gel eluted with chloroform afforded the trioxane **1f** (0.211 g, 0.85 mmol, 49%) as an oil. An analytical sample was obtained by Kugelrohr distillation at 60–70 °C (5×10^{-4} mm): IR (CCl_4) ν_{max} 1695, 1645 cm^{-1}; NMR (CCl_4) δ 0.33–0.77 (m, 8 H); 0.80–1.33 (m, 2 H), 3.75 (s, 2 H), 6.22 (d, J = 11 Hz, 2 H), 7.03 (d, J = 11 Hz, 2 H); mass spectrum, m/e 248 (M^+). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.88; H, 6.46.

Irradiation of *p*-Benzoquinone with *tert*-Butylethylene. Under 1 Atm of Oxygen. A solution of 1.317 g (12.2 mmol) of *p*-benzoquinone and 4.414 g (52.5 mmol) of *tert*-butylethylene in 450 mL of carbon tetrachloride saturated with oxygen and cooled with a cold finger was irradiated with the CR-8 for 4.5 h with rapid stirring. Chromatography on 60 g of silica gel eluted initially with benzene afforded first the trioxane **1g** (0.674 g, 3.05 mmol, 25%). After recrystallization from ether–pentane **1g** showed the following: mp 78.4–78.7 °C; IR ($CHCl_3$) ν_{max} 1690, 1640 cm^{-1}; NMR (CCl_4) δ 1.03 (s, 9 H), 4.00 (m, 3 H), 6.26 (m, 3 H), 7.45 (m, 1 H); mass spectrum, m/e 224 (M^+). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.45; H, 7.12.

Next, a mixture of oxetanes **11** and **12** (1.62 g, 8.4 mmol, 69%) was eluted from the column with chloroform. Attempts to separate these oxetanes by extensive thick-layer chromatography were not successful. The mixture of oxetanes **11** and **12** showed the following: IR (CCl_4) ν_{max} 1670, 1640 cm^{-1}; NMR (CCl_4) δ 0.88 (s), 0.90 (s), 2.60 (2 overlapping dd, J = 6 and 3 Hz), 3.20 (dd, J = 9 and 9 Hz), 4.60 (m), 6.28 (m), 7.30 (m). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.84; H, 8.39.

The relative yields of the trioxane **1g** and the oxetanes **11** and **12** were determined by the above procedure at various oxygen pressures and are displayed in Figure 2. Although these solutions were allowed to approach oxygen equilibrium prior to irradiation, no special precautions were taken to ensure that oxygen equilibrium had been established. The ratio of oxetanes was determined by NMR; **12**:**11** equals the ratio of one-half the integral of the δ 2.60 pattern (methylene protons of **12**) to the integral of the δ 3.20 pattern (methinyl proton of **11**).

Under 11 Atm of Oxygen. A solution of 0.104 g (0.96 mmol) of *p*-benzoquinone and 0.3 g (3.57 mmol) of *tert*-butylethylene in 45 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 11 atm with oxygen was irradiated with the CR-8 for 0.5 h. The aforementioned isolation procedure yielded the trioxane **1g** (0.142 g, 0.64 mmol, 66%) and a mixture of oxetanes **11** and **12** (0.047 g, 0.24 mmol, 25%).

Irradiation of *p*-Benzoquinone with Cyclohexene. Under 11 Atm of Oxygen. A solution of 0.651 g (6.03 mmol) of *p*-benzoquinone and 1.22 g (14.8 mmol) of cyclohexene in 80 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 11 atm with oxygen was irradiated with the CR-8 for 2 h. Chromatography on a column of ~100 g of silica gel eluted with benzene–chloroform (75:25) afforded the trioxane **1h** (0.782 g, 3.52 mmol, 58%). An analytical sample was obtained as an oil by distillation at 95 °C (10^{-6} mm): IR (CCl_4) ν_{max} 1680, 1640 cm^{-1}; NMR (CCl_4) δ 1.20–2.20 (m, 8 H), 4.00 (m, 2 H), 6.34 (m, 3 H), 7.67 (dd, J = 10 and 3 Hz, 1 H). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.61; H, 6.27.

Under 1 Atm of Oxygen. A solution of 0.167 g (1.55 mmol) of *p*-benzoquinone and 0.810 g (9.88 mmol) of cyclohexene in 70 mL of carbon tetrachloride saturated with oxygen and cooled with a cold finger was irradiated with the CR-8 for 1.25 h. Isolation as above afforded the trioxane **1h** (0.099 g, 0.45 mmol, 29%).

Irradiation of 2,6-Dimethyl-*p*-benzoquinone with Cyclohexene and Oxygen. A solution of 0.181 g (1.33 mmol) of 2,6-dimethyl-*p*-benzoquinone and 1.21 g (14.67 mmol) of cyclohexene in 40 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 12 atm of oxygen was irradiated with the CR-8 (3.3 W) for 0.5 h. Chromatography on a column of 30 g of silica gel eluted with chloroform yielded **1i**. After recrystallization from ether–pentane the trioxane **1i** (0.192 g, 0.769 mmol, 59%) showed the following: mp 81.3–82.5 °C; IR ($CHCl_3$) ν_{max}

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1670, 1650 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.8 (m, 8 H), 1.9 (br s, 6 H), 3.6–4.6 (m, 2 H), 6.3 (m, 1 H), 7.5 (m, 1 H); mass spectrum, *m/e* 250 (M^+). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.70; H, 7.41.

Irradiation of *p*-Benzoquinone with Cyclooctene and Oxygen. A solution of 0.15 g (1.38 mmol) of *p*-benzoquinone and 0.847 g (7.70 mmol) of cyclooctene in 38 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 11 atm with oxygen was irradiated with the CR-8 for 45 min. Chromatography on a column of about 20 g of silica gel eluted with benzene removed the unreacted cyclooctene and *p*-benzoquinone. The oxetane and trioxane **1j** were eluted together with benzene–chloroform (50:50) and rechromatographed on silica gel thick-layer plates eluted with benzene–methanol (95:5). The trioxane **1j** was obtained as an oil (0.043 g, 0.18 mmol, 13%). An analytical sample was obtained by distillation at 95 °C (10^{-6} mm): IR (CCl_4) ν_{max} 1675, 1630 cm^{-1}; NMR (CCl_4) δ 1.65 (m, 10 H), 4.20 (m, 2 H), 6.20 (m, 2 H), 6.67 (m, 1 H), 7.50 (m, 1 H); mass spectrum, *m/e* 250 (M^+). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.23; H, 7.29.

The oxetane was obtained as an oil (0.1687 g, 0.77 mmol, 78%) and had spectral properties identical with those described by Bryce-Smith.[15]

Irradiation of *p*-Benzoquinone with Norbornene and Oxygen. A solution of 0.362 g (3.35 mmol) of *p*-benzoquinone and 0.348 g (3.69 mmol) of norbornene in 30 mL of carbon tetrachloride at −10 °C in a Griffin–Worden tube pressurized to 13 atm with oxygen was irradiated with the 488.0-nm line of the CR-18 (7 W) for 30 min. A precipitate that formed during the irradiation was removed by filtration and the filtrate evaporated to dryness. The residue was flash chromatographed[47] on a 38-mm diameter column eluted with ethyl acetate–petroleum ether (30–60 °C) (15:85 to 30:70) to yield *p*-benzoquinone (0.032 g, 0.30 mmol), trioxane **1k** (0.146 g, 0.62 mmol, 20% based on recovered starting material), and the *exo*-oxetane (0.100 g, 0.49 mmol, 16% based on recovered starting material). An analytical sample of the trioxane **1k** was obtained by distillation in a Kulgerohr at 70 °C (10^{-4} mm) followed by recrystallization from ether–pentane: mp 66.4–67.6 °C; IR ($CHCl_3$) ν_{max} 1695, 1675, 1640 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 0.93–1.77 (m, 5 H), 1.97–2.33 (m, 3 H), 3.77 (br d, J = 4.5 Hz, 1 H), 4.41 (dd, J = 1.5 and 4.5 Hz, 1 H), 6.12 (dd, J = 2.0 and 11 Hz, 1 H), 6.17 (dd, J = 2.0 and 11 Hz, 1 H), 6.71 (dd, J = 3.5 and 11 Hz, 1 H), 7.05 (dd, J = 3.5 and 11 Hz, 1 H); mass spectrum, *m/e* 234 (M^+). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.53; H, 6.05.

The stereochemistry of trioxane **1k** is *exo*-ether and *endo*-peroxide. The degradative work that lead to this assignment will be described in a subsequent paper.[22] The *exo*-oxetane had spectroscopic properties identical with those previously described.[48]

Irradiation of *p*-Benzoquinone with Vinyl Acetate and Oxygen. A solution of 0.326 g (3.02 mmol) of *p*-benzoquinone and 0.932 g (10.8 mmol) of vinyl acetate in 35 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 11 atm of oxygen was irradiated with the CR-8 for 1.0 h. Chromatography on silica gel thick-layer plates afforded two bands. The more polar band was found to be a mixture of oxetanes (0.172 g, 0.88 mmol, 30%), which could not be separated by extensive chromatography. An analytical sample of the mixture was obtained by distillation at 73 °C (10^{-6} mm): NMR (CCl_4) δ 2.05 (s), 2.13 (dd, J = 4 and 13 Hz), 3.23 (dd, J = 5 and 13 Hz), 4.80 (m), 5.53 (t, J = 7 Hz), 6.15 (m), 6.51 (dd, J = 4 and 5 Hz), 7.20 (m). Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.86; H, 5.20.

The less-polar band was found to be a mixture of trioxanes **1l** and **1m** (0.256 g, 1.13 mmol, 38%). Attempted separation by extensive chromatography (10 elutions with benzene on silica gel thick-layer plates) led to the decomposition of **1l**. However, trioxane **1m** could be obtained from the thick-layer plates in pure form after all of the **1l** had decomposed. An analytical sample of trioxane **1m** was obtained as an oil by distillation at 75 °C (10^{-6} mm): IR (CCl_4) ν_{max} 1755, 1680, 1640 cm^{-1}; NMR (CCl_4) δ 2.14 (s, 3 H), 4.11 (dd, J = 1.5 and 13 Hz, 1 H), 4.74 (dd, J = 3 and 13 Hz, 1 H), 6.1–6.8 (m, 3 H), 7.50 (dd, J = 3 and 10 Hz, 1 H); mass spectrum, *m/e* 226 (M^+). Anal. Calcd for $C_{10}H_{10}O_6$: C, 53.10; H, 4.46. Found: C, 53.15; H, 4.50.

The NMR spectrum of the isomeric trioxane **1l** as determined by a difference spectrum between the NMR spectrum of the mixture of trioxanes and the NMR spectrum of pure **1m** was as follows: δ 2.14 (s), 3.83 (dd, J = 5 and 12 Hz), 4.29 (dd, J = 5 and 18 Hz), 6.1–6.8 (m), 7.26 (dd, J = 4 and 11 Hz).

Attempts to distill mixtures of the trioxanes **1l** and **1m** led to the decomposition of **1l** and the formation of *p*-benzoquinone and the known[27] spirolactone **21**. Spirolactone **21** was isolated as an oil by silica gel thick-layer chromatography: IR (CCl_4) ν_{max} 1810, 1670 cm^{-1}; NMR ($CDCl_3$) δ 4.48 (s, 2 H), 6.31 (d, J = 10 Hz, 2 H), 6.71 (d, J = 10 Hz, 2 H); mass spectrum, *m/e* 166 (M^+), 122 ($M^+ - CO_2$).

Irradiation of *p*-Benzoquinone and 2,2-Dimethyl-3-(trimethylsiloxy)-3-butene and Oxygen. A solution of 0.510 g (4.720 mmol) of *p*-benzoquinone and 1.67 g (9.679 mmol) of 2,2-dimethyl-3-(trimethylsiloxy)-3-butene[49] in 35 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 11 atm with oxygen was irradiated with the CR-8 (6 W) for 2.5 h. Upon concentration the resulting dark-orange oil crystallized under high vacuum. Recrystallization from ether–petroleum ether afforded trioxane **1n** (0.972 g, 3.12 mmol, 66%) as colorless prisms: mp 70.4–71.3 °C; IR (KBr) ν_{max} 1695, 1642 cm^{-1}; NMR (CCl_4) δ 0.20 (s, 9 H), 1.02 (s, 9 H), 3.53 (d, J = 12 Hz, 1 H), 4.03 (d, J = 12 Hz, 1 H), 6.10 (br s, 1 H), 6.26 (br s, 1 H), 6.67 (dd, J = 3 and 10 Hz, 1 H), 7.06 (dd, J = 3 and 10 Hz, 1 H). Anal. Calcd for $C_{15}H_{24}O_5Si$: C, 57.66; H, 7.74. Found: C, 57.89; H, 7.86.

Irradiation of *p*-Benzoquinone and 1-Phenyl-1-(trimethylsiloxy)-ethylene and Oxygen. A solution of 0.611 g (5.655 mmol) of *p*-benzoquinone and 1.171 g (6.984 mmol) of 1-phenyl-1-(trimethylsiloxy)-ethylene[49] in 35 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 11 atm with oxygen was irradiated with the CR-8 (6 W) for 5 h. Upon concentration the resulting dark-orange oil crystallized during 48 h under high vacuum. Recrystallization from ether–pentane afforded trioxane **1o** (1.47 g, 4.43 mmol, 78%) as pale-yellow prisms: mp 65.4–65.8 °C; IR ($CHCl_3$) ν_{max} 1690 cm^{-1}; NMR (CCl_4) δ 0.80 (s, 9 H), 3.90 (s, 2 H), 6.13 (br s, 1 H), 6.30 (br s, 1 H), 6.63 (br s, 1 H), 6.86 (br s, 1 H), 7.20–7.70 (m, 5 H). Anal. Calcd for $C_{17}H_{20}O_5Si$: C, 61.42; H, 6.06. Found: C, 61.67; H, 6.21.

Irradiation of 3-Methyl-2-butenyl-*p*-benzoquinone and Oxygen. With a High Pressure Xenon–Mercury Arc. a Solution of 0.140 g (0.795 mmol) of 3-methyl-2-butenyl-*p*-benzoquinone[50] in ~40 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 11 atm with oxygen was irradiated at room temperature with the filtered output of a Hanovia 1000-W xenon–mercury arc for 24 h. The output from the arc was passed first through 10 cm of a $CuSO_4$ solution (0.44 g of $CuSO_4 \cdot 5H_2O$, 100 mL of 2.7 M ammonium hydroxide) and then through 10 cm of a $NaNO_2$ solution (7.5 g of $NaNO_2$, 100 mL of water).[51a] Chromatography on silica gel thick-layer plates eluted with chloroform–methanol (97:3) afforded the trioxane **1p** that was recrystallized from methylene chloride–ether to obtain 0.060 g (0.288 mmol, 36%) of colorless crystals: mp 96.4–96.5 °C; IR ($CHCl_3$) ν_{max} 3040, 1690, 1660, 1625 cm^{-1}; NMR ($CDCl_3$) δ 1.14 (s, 3 H), 1.73 (s, 3 H), 2.81–3.41 (m, 2 H), 4.39 (dd, J = 5 and 1.5 Hz, 1 H), 6.20 (d, J = 2 Hz, 1 H), 6.30 (dd, J = 10 and 2 Hz, 1 H), 6.80 (d, J = 10 Hz, 1 H); mass spectrum, *m/e* 208 (M^+), 176 ($M^+ - O_2$). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.67; H, 5.77.

With an Argon Laser at Room Temperature. A solution of 0.457 g (2.60 mmol) of 3-methyl-2-butenyl-*p*-benzoquinone was irradiated under the aforementioned conditions by using the CR-8 for 3 h. The usual isolation and purification afforded 0.291 g (1.40 mmol, 54%) of trioxane **1p**.

With an Argon Laser at −80 °C. A solution of 0.350 g (1.99 mmol) of 3-methyl-2-butenyl-*p*-benzoquinone in ~40 mL of $CFCl_3$ was cooled in a dry ice–isopropyl alcohol bath (−80 °C) and irradiated with the CR-8 as described above for 3 h. The usual isolation and purification afforded 0.406 g (1.95 mmol, 98%) of trioxane **1p**.

Irradiation of 2-Methyl-3-(3-methyl-2-butenyl)-1,4-naphthoquinone (Menaquinone-1; MK-1) and Oxygen. A solution of 0.125 g (0.52 mmol) of MK-1[52] in 35 mL $CFCl_3$ cooled to −30 °C in a Griffin–Worden tube pressurized to 12 atm with oxygen was irradiated with the 457.9-nm line of the CR-18 (1.5 W) for 2 h. Chromatography of the residue on a silica gel column eluted with chloroform afforded the trioxane **1q** (0.044 g, 0.16 mmol, 31%). An analytical sample was obtained by recrystallization from chloroform–carbon tetrachloride: mp 164–165 °C; IR ($CHCl_3$) ν_{max} 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 3 H), 1.76 (s, 3 H), 1.98 (t, J = 1 Hz, 3 H), 2.60–3.30 (m, 2 H), 4.39 (dd, J = 1 and 6 Hz, 1 H), 7.58 (m, 3 H), 8.00 (m, 1 H); ^{13}C NMR ($CDCl_3$, ppm downfield from Me_4Si) 12.24, 22.48, 22.70, 30.45, 81.21, 102.28, 126.44, 127.26, 128.77, 130.51, 130.62, 131.97, 132.35, 133.54, 152.18, 184.84; mass spectrum, *m/e* 272 (M^+), 240 ($M^+ - O_2$), 225 ($M^+ - O_2 - CH_3$), 186 (base, $M^+ - (CH_3)_2CO - CO$). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.21; H, 5.87.

The crystalline allylic hydroperoxide **29**[33] was also isolated (0.048 g, 0.176 mmol, 34%): mp 92–93 °C; IR ($CHCl_3$) ν_{max} 3550, 3430, 1670,

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1602, 1300 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 6 H), 2.20 (s, 3 H), 6.50 (s, 2 H), 7.50–8.15 (m, 4 H), 8.39 (s, 1 H); ^{13}C NMR ($CDCl_3$, δ ppm downfield from Me_4Si) 13.42, 24.06, 82.42, 121.40, 126.00, 126.16, 131.72, 131.92, 133.35, 140.48, 142.49, 145.44, 184.29, 184.97; mass spectrum, m/e 272 (M^+), 240 ($M^+ - O_2$), 239 ($M^+ - O_2H$).

Irradiation of 2-Methoxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone (Methyl Lapachol) and Oxygen. A solution of 0.140 g (0.55 mmol) of methyl lapachol[53] in 35 mL of $CFCl_3$ cooled to −30 °C in a Griffin–Worden tube pressurized to 12 atm with oxygen was irradiated with the 457.9-nm line of the CR-18 (1.5 W) for 2 h. Flash chromatography[47] on a silica gel column eluted with ethyl acetate–petroleum ether (15:85) afforded the trioxane **1r** (0.041 g, 0.142 mmol, 26%); after recrystallization from ether: mp 144–145 °C; IR ($CHCl_3$) ν_{max} 1675 cm^{-1}; NMR ($CDCl_3$) δ 1.16 (s, 3 H), 1.78 (s, 3 H), 2.98–3.50 (m, 2 H), 4.00 (s, 3 H), 4.43 (dd, J = 6 and 2 Hz, 1 H), 7.49–8.20 (m, 4 H); mass spectrum, m/e 288 (M^+), 256 ($M^+ - O_2$). Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.82; H, 5.68.

Irradiation of Benzophenone with Cyclohexene and Oxygen. A solution of 0.263 g (1.45 mmol) of benzophenone and 1.26 g (15.36 mmol) of cyclohexene in 40 mL of carbon tetrachloride in a Griffin–Worden tube pressurized to 13 atm with oxygen was irradiated with all of the ultraviolet lines of the CR-18 (2.5 W) for 24 h. Chromatography on a column of 40 g of silica gel eluted with chloroform afforded the trioxane **2a**, which had after recrystallization from ether–pentane (0.041 g, 0.138 mmol, 10%): mp 148.2–150.5 °C; IR ($CHCl_3$) ν_{max} 3100–2860, 1490 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.2 (m, 8 H), 3.4–4.5 (m, 2 H), 7.2–7.4 (m, 10 H); mass spectrum, m/e 296 (M^+). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.10; H, 6.90.

Irradiation of Benzophenone with Norbornene and Oxygen. A solution of 0.182 g (1.0 mmol) of benzophenone and 0.329 g (3.5 mmol) of norbornene in 15 mL of $CFCl_3$ at 10 °C in a Griffin–Worden tube pressurized to 11 atm with oxygen was irradiated with the filtered output of a Hanovia 1000-W xenon–mercury arc for 80 h. The output from the arc was passed first through an Oriel glass filter (G774-3554), then through an Oriel infrared-absorbing glass filter (G776-7100), and finally through a 10-cm cell of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate[51b] (0.02 g/10 mL of water). Chromatography on thick-layer plates eluted with benzene afforded unreacted benzophenone (0.168 g, 0.923 mmol, 92%), the oxetane (0.009 g, 0.033 mmol, 3%, 43% based on recovered benzophenone), and the trioxane **2b** (0.0107 g, 0.0347 mmol, 3%, 45% based on recovered benzophenone). After recrystallization from pentane **2b** showed the following: mp 93.7–94.0 °C; IR (KBr) ν_{max} 2900, 1450 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.7 (m, 5 H), 2.2 (br s, 1 H), 2.5 (br s, 1 H), 3.8 (d, J = 2.5 Hz, 1 H), 4.5 (d, J = 2.5 Hz, 1 H), 7.2–7.7 (m, 10 H); mass spectrum, m/e 308 (M^+). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.89; H, 6.53. Found: C, 78.10; H, 6.57.

Irradiation of *p*-Benzoquinone with *tert*-Butylethylene and Sulfur Dioxide. A solution of 0.653 g (7.77 mmol) of *tert*-butylethylene, 0.209 g (1.93 mmol) of *p*-benzoquinone in 10 mL of dry carbon tetrachloride (passed through a column of Woelm alumina), and ~2 mL of liquid sulfur dioxide in a 25-mL dry round-bottom flask fitted with a dry ice–acetone condenser was maintained at −11 °C by the refluxing sulfur dioxide. Irradiation of this solution with the CR-8 (~2 W) for 10 min afforded the sulfone **3a** as a colorless precipitate. The volatile components were removed under reduced pressure and the residue triturated with carbon tetrachloride to produce more of the colorless solid. This solid was collected by filtration to afford 0.402 g (1.57 mmol, 81%) of **3a**. An analytical sample was obtained by recrystallization from ethanol: mp 254.0–255.2 °C; IR (KBr) ν_{max} 3400, 2970, 1270, 1225, 1130 cm^{-1}; NMR (acetone-d_6) δ 0.95 (s, 9 H), 3.37 (dd, J = 8 and 4 Hz, 1 H), 4.73 (m, 2 H), 6.98 (m, 2 H), 7.17 (m, 1 H), 8.57 (s, 1 H); mass spectrum, m/e 256 (M^+). Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29; S, 12.51. Found: C, 56.18; H, 6.20; S, 12.59.

Irradiation of *p*-Benzoquinone with Cyclohexene and Sulfur Dioxide. A solution of 0.405 g (4.93 mmol) and 0.206 g (1.91 mmol) of *p*-benzoquinone was irradiated in the manner described in the preceding section to afford, after chromatography on silica gel thick-layer plates eluted with chloroform, the sulfone **3b**. Recrystallization from chloroform–benzene yielded analytically pure **3b** (0.281 g, 1.11 mmol, 58%): mp 171.0–173.9 °C; IR ($CHCl_3$) ν_{max} 3580, 3350, 3000, 1290, 1130 cm^{-1}; NMR ($CDCl_3$) δ 1.17–2.67 (m, 8 H), 3.33 (m, 1 H), 4.50 (m, 1 H), 6.30 (m, 1 H), 6.93 (m, 2 H), 7.34 (d, J = 3 Hz, 1 H); mass spectrum, m/e 253 (M^+). Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.68; H, 5.55; S, 12.61. Found: C, 56.76; H, 5.65; S, 12.63.

Irradiation of *p*-Benzoquinone with Vinyl Acetate and Sulfur Dioxide. A solution of 0.932 g (10.6 mmol) of vinyl acetate and 0.197 g (1.81 mmol) of *p*-benzoquinone was irradiated for 20 min as described above to afford, after chromatography on silica gel thick-layer plates eluted with chloroform–methanol (96:4) two sulfones, **3c** and **3d** (0.1795 g, 0.65 mmol), and the two oxetanes (0.0371 g, 0.19 mmol, 11%). NMR analysis of the mixture of sulfones indicated that the ratio of **3c**:**3d** was 56:44 (20%:16%). The sulfone **3c** was obtained by fractional recrystallization of the sulfone mixture from chloroform–acetone: mp 182.9–184.5 °C; IR (KBr) ν_{max} 3420, 1755, 1295, 1135 cm^{-1}; NMR (acetone-d_6) δ 2.12 (s, 3 H), 4.90 (m, 2 H), 6.00 (m, 1 H), 7.02 (m, 2 H), 7.34 (d, J = 2 Hz, 1 H), 8.63 (br s, 1 H); mass spectrum, m/e 258 (M^+). Anal. Calcd for $C_{10}H_{10}O_6S$: C, 46.51; H, 3.90; S, 12.42. Found: C, 46.40; H, 3.82; S, 12.42.

The sulfone **3d** was obtained by chromatography of the mother liquors from the aforementioned fractional recrystallization on silica gel thick-layer plates eluted 10 times with chloroform–acetone (98:2) followed by recrystallization from chloroform–acetone: mp 164.1–169.2 °C; IR (KBr) ν_{max} 3400, 1755, 1290, 1130 cm^{-1}; NMR (acetone-d_6) δ 2.10 (s, 3 H), 3.98 (m, 2 H), 6.77 (dd, J = 3 and 4 Hz, 1 H), 7.08 (m, 2 H), 7.21 (d, J = 3 Hz, 1 H), 8.75 (br s, 1 H); mass spectrum, m/e 258 (M^+). Anal. Calcd for $C_{10}H_{10}O_6S$: C, 46.51; H, 3.90; S, 12.42. Found: C, 46.72; H, 3.78; S, 12.47.

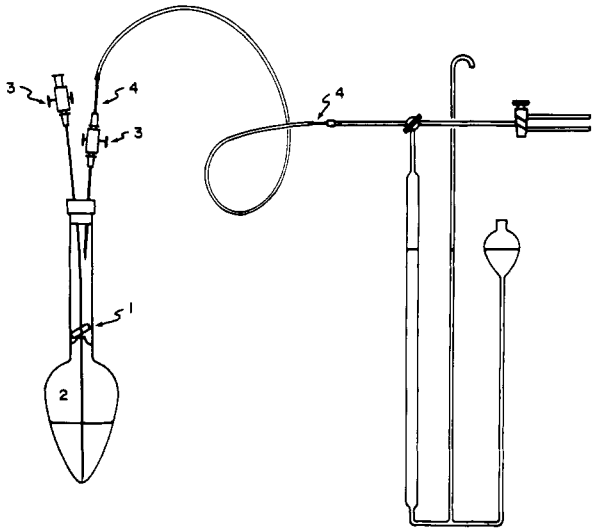

Figure 4. A simple apparatus for oxygen-18 labeling studies at atmospheric pressure. See experimental description for key to apparatus component labels.

Thermal Fragmentation of Trioxanes. A solution of the trioxane and an internal standard was injected onto a 12 ft × 0.25 in. 5% SE-30 on Chromasorb W GLC column with an injection port temperature of 260 °C. The trioxanes fragmented completely in the injection port. The fragmentation products were collected and identified by comparison of retention times and mass spectra with those of authentic samples.

Trioxane 1b. With diphenylacetylene as an internal standard, the yields of the pyrolysis products of **1b** were determined to be *p*-benzoquinone 76.5% and benzaldehyde 41%. Trioxane **1b** was stable in refluxing benzene for 4 h and decomposed only slightly in refluxing toluene after 5 h.

Trioxane 1d. With diphenylacetylene as an internal standard, the yields of the pyrolysis products of **1d** were determined to be *p*-benzoquinone 54% and benzophenone 65%. Trioxane **1d** decomposed to the same products upon standing in solution for several weeks at room temperature.

Trioxane 1g. With naphthalene as an internal standard, the yields of the pyrolysis products of **1g** were determined to be *p*-benzoquinone 7% and pivaldehyde 17%.

Oxygen-18 Labeling Studies. The apparatus used for the oxygen-18 labeling experiments is illustrated in Figure 4. A small magnet (1) was inserted into a 250-mL flask containing 50% enriched $^{18}O_2$ (2) (Wilmad Glass Co.) and the flask sealed with a septum. A long and a short syringe needle were inserted through the septum. Both needles were capped with "Mininert" Teflon syringe valves (3) (Precision Scientific). The short needle was connected to a gas manometer with Luer adapters (4) and Teflon tubing with Luer ends. The vapor space was filled with argon and throughout the useful lifetime of the $^{18}O_2$ sample the pressure on the system was maintained at 1 atm by adding argon. The breakseal in the flask was then broken with the magnetic bar. Solutions to be irradiated were first flushed with argon and introduced into the bottom of the flask through the long needle that had been inserted through the breakseal. The solutions were irradiated with the visible lines of the argon laser in

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the usual fashion and removed through the long needle upon bleaching of the *p*-benzoquinone. The flask was rinsed several times with fresh solvent between runs. This apparatus provides a relatively cheap and convenient way of introducing $^{18}O_2$ into the trioxanes and can be used for at least five reactions on a 2-mmol scale over the course of several days without appreciable dilution of the $^{18}O_2$ with $^{16}O_2$.

Oxygen-18 labeled trioxanes **1b**, **1d**, and **1g** were prepared in this apparatus and isolated by silica gel thick-layer chromatography as described in the appropriate sections above. The trioxanes were pyrolyzed in the injection port of a gas chromatograph as described in the previous section, the pyrolysis products were collected, and the extent of oxygen-18 incorporation into the pyrolysis products was determined by mass spectrometry. The results of these experiments are recorded in Table III.

Decomposition of Trioxanes with Azide and Iodide Ions. Trioxane 1b. To a solution of 0.108 g (0.44 mmol) of trioxane **1b** in 5 mL of acetone and 1.5 mL of water was added 0.094 g (1.44 mmol) of sodium azide with stirring at room temperature. After 0.5 h the acetone was removed and 10 mL of water added to the black concentrate. The resulting suspension was extracted with ether (3 × 30 mL) and the ether extract dried and evaporated. The residue was chromatographed on a silica gel thick-layer plate eluted with benzene–ethanol (97:3) to afford 0.0446 g (0.33 mmol, 75%) of α-hydroxyacetophenone; after sublimation at 50 °C: mp 86.4–87.1 °C (lit.[54] 86–87 °C); IR ($CHCl_3$) ν_{max} 3475, 3010, 1690 cm^{-1}; NMR (acetone-d_6) δ 4.2 (br s, 1 H), 5.0 (s, 2 H), 7.7 (m, 3 H), 8.15 (m, 2 H). Hydroquinone was also isolated and, in a control experiment, shown to arise from the reduction of *p*-benzoquinone by azide ion.

Trioxane **1b** afforded α-hydroxyacetophenone in 33% yield and *p*-benzoquinone upon treatment with sodium iodide in acetone for 71 h.

Trioxane 1d. To a solution of 0.101 g (0.31 mmol) of trioxane **1d** in 6 mL of acetone and 1 mL of water was added 0.078 g (1.20 mmol) of sodium azide with stirring at room temperature. After 49 h the acetone was removed and 10 mL of water added. The black suspension was extracted with ether (2 × 30 mL) and the ether extract dried and evaporated. The residue was chromatographed on a silica gel thick-layer plate eluted with benzene to yield 0.033 g (0.10 mmol) of unreacted trioxane **1d** and 0.0125 g (0.07 mmol, 33% based upon recovered starting material) of benzophenone and hydroquinone.

To a solution of 0.080 g (0.25 mmol) of trioxane **1d** in 8 mL of acetone was added 0.961 g (0.64 mmol) of sodium iodide. The solution was stirred vigorously and heated at 48 °C for 50 h. Chromatography on a silica gel thick-layer plate eluted with benzene–methanol (98:2) afforded *p*-benzoquinone, 0.0084 g (0.046 mmol, 18%) of benzophenone, and 0.0223 g (0.10 mmol, 42%) of 1,1-diphenylethanediol: mp 121.1–121.4 °C (lit.[55] mp 122 °C); IR ($CHCl_3$) ν_{max} 3585 cm^{-1}; NMR ($CDCl_3$) δ 2.10 (br s, 1 H), 3.35 (br s, 1 H), 4.15 (s, 2 H), 7.40 (m, 10 H).

Photodecomposition of the Menaquinone-1 Trioxane (1q). Isolation of the Acetone Fragment. A solution of 0.035 g (0.130 mmol) of menaquinone-1 trioxane (**1q**) was dissolved in 1 mL of deuteriochloroform in an NMR tube and irradiated at 20 °C with the ultraviolet output of the CR-18 (2.8 W). The reaction was followed by NMR until the trioxane had been consumed. The yield of acetone formed in the fragmentation was determined to be 89% with 0.0085 g (0.078 mmol) of *p*-benzoquinone as an internal standard.

In a second experiment, the acetone was isolated as its 2,4-DNP derivative as follows: A solution of 0.115 g (0.422 mmol) of menaquinone-1 trioxane (**1q**) in 25 mL of methylene chloride in a Griffin–Worden tube under argon was irradiated by using all of the ultraviolet lines of the CR-18 (2.8 W) at 0 °C for 2.5 h, during which time complete decomposition of the trioxane was observed. The Griffin–Worden tube was connected to a vacuum trap that was cooled in a liquid nitrogen–methanol bath. The volatile contents of the Griffin–Worden tube were collected by trap-to-trap distillation at 0.1 mm. The distillate was treated with a solution of 0.100 g (0.51 mmol) of 2,4-dinitrophenylhydrazine in 40 mL of methanol and 15 drops of concentrated hydrochloric acid. After stirring overnight at 50 °C, the solvent was removed by evaporation to afford a crystalline residue that was chromatographed on a column of 35 g of silica gel eluted with toluene to yield 0.047 g (0.197 mmol, 47%) of the 2,4-DNP derivative of acetone. The recrystallized material (ethanol) had an undepressed mixture melting point (124.8–125.7 °C) with authentic material.

Isolation of the Aldehyde 30. A solution of 0.086 g (0.316 mmol) of menaquinone-1 trioxane (**1q**) in 25 mL of chloroform in a quartz Griffin–Worden tube under argon was irradiated with all of the ultraviolet lines of the CR-18 (2.8 W) at 0 °C for 35 min. The tube was rotated frequently to avoid burning the contents onto the inner wall. Evaporation of the solvent and chromatography of the residue on 15 g of silica gel eluted with chloroform afforded 0.017 g (0.086 mmol, 24%) of **30** as a yellow oil. This substance was identical with authentic material (vide infra) as judged by comparison of NMR and IR spectra and R_f characteristics from thin-layer chromatography.

Preparation of 2-Methyl-3-(2-hydroxyethyl)-1,4-dimethoxynaphthalene. To a solution of 3.04 g (10.8 mmol) of 2-bromo-3-methyl-1,4-dimethoxynaphthalene[56] in 25 mL of anhydrous tetrahydrofuran at −78 °C under nitrogen was added with stirring 6.76 mL of 1.6 M *n*-butyllithium in hexane (10.8 mmol). After 0.5 h, a solution of 0.525 g (11.9 mmol) of ethylene oxide in 5 mL of anhydrous tetrahydrofuran was added. The reaction mixture was allowed to warm to room temperature, and the reaction was quenched by the addition of water after 16 h. The mixture was extracted with ether and the ether layer dried and evaporated. The residual oil was purified by flash column chromatography[47] on silica gel eluted with ethyl acetate–pentane (30:70) to yield 1.84 g (7.47 mmol, 69%) of the alcohol as colorless needles. An analytical sample was obtained by recrystallization from chloroform–pentane and Kugelrohr distillation at 65 °C (0.002 mm): mp 73–74 °C; IR ($CHCl_3$) ν_{max} 3630, 3020, 1595, 1355 cm^{-1}; NMR ($CDCl_3$) δ 2.35 (br s, 1 H), 2.40 (s, 3 H), 3.15 (t, J = 7 Hz, 2 H), 3.85 (t, J = 7 Hz, 2 H), 3.90 (s, 3 H), 3.95 (s, 3 H), 7.30–7.60 (m, 2 H), 7.85–8.25 (m, 2 H); mass spectrum, m/e 246 (M^+). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.30; H, 7.43.

Preparation of 2-Methyl-3-(2-hydroxyethyl)-1,4-naphthoquinone. To a solution of 1.2 g (4.8 mmol) of 2-methyl-3-(2-hydroxyethyl)-1,4-dimethoxynaphthalene in 72 mL of dioxane and 5 mL of water was added 1.8 g (14.5 mmol) of argentic oxide.[57] To this suspension was added 2.43 mL of 6.2 N nitric acid (15.0 mmol). The mixture was stirred until it became homogeneous and then partitioned between petroleum ether (250 mL) and water (50 mL). The organic phase was washed with water (2 × 35 mL), dried, and evaporated. Recrystallization of the residue from ether–pentane yielded 0.861 g (3.99 mmol, 82%) of the naphthoquinone as yellow needles: mp 122.5–123.5 °C; IR ($CHCl_3$) ν_{max} 3640, 3035, 1670, 1615, 1305 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (s, 3 H), 2.40 (br s, 1 H), 2.95 (t, J = 7 Hz, 2 H), 3.80 (t, J = 7 Hz, 2 H), 7.50–7.80 (m, 2 H), 7.85–8.15 (m, 2 H); mass spectrum, m/e 216 (M^+). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.04; H, 5.57.

Preparation of 2-Methyl-3-(2-oxoethyl)-1,4-naphthoquinone (30). To a solution of 0.317 g (1.4 mmol) of 2-methyl-3-(2-hydroxyethyl)-1,4-naphthoquinone in 10 mL of dry methylene chloride was added 0.036 g (0.44 mmol) of anhydrous sodium acetate and 0.396 g (2.2 mmol) of pyridinium chlorochromate.[58] The reaction mixture was stirred at room temperature for 3.5 h and then diluted with 50 mL of ether. The resulting solid was removed by filtration through a bed of Celite and silica gel and the filtrate evaporated. The residue was flash chromatographed[47] on a silica gel column eluted with petroleum ether–ethyl acetate followed by Kugelrohr distillation at 60 °C (0.002 mm) to yield 0.288 g (1.36 mmol, 92%) of **30** as yellow prisms: mp 109–110 °C; IR ($CHCl_3$) ν_{max} 3040, 1760, 1670, 1605, 1385, 1300 cm^{-1}; NMR ($CDCl_3$) δ 2.15 (s, 3 H), 3.85 (br s, 2 H), 7.55–7.85 (m, 2 H), 7.90–8.20 (m, 2 H), 9.75 (br s, 1 H); mass spectrum, m/e 214 (M^+), 186 ($M^+ - CO$). Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.91; H, 4.67.

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Registry No. 1a, 81741-08-4; **1b**, 53696-88-1; **1c**, 81741-09-5; **1d**, 53696-89-2; **1e**, 81741-10-8; **1f**, 81741-11-9; **1g**, 53696-90-5; **1h**, 54265-46-2; **1i**, 81741-12-0; **1j**, 81741-13-1; **1k**, 81741-14-2; **1l**, 54265-47-3; **1m**, 81741-15-3; **1n**, 81741-16-4; **1o**, 81741-17-5; **1p**, 81741-18-6; **1q**, 76670-42-3; **1r**, 81768-77-6; **2a**, 81741-19-7; **2b**, 81741-20-0; **3a**, 54265-42-8; **3b**, 54265-48-4; **3c**, 54265-43-9; **3d**, 54265-44-0; **4**, 81741-21-1; **6**, 81741-22-2; **7**, 81741-23-3; **8**, 35756-94-6; **11**, 81741-24-4; **12**, 81741-25-5; **21**, 4385-47-1; **28**, 957-78-8; **29**, 78828-09-8; **30**, 76670-43-4; O_2, 7782-44-7; SO_2, 7446-09-5; cyclooctatetraene, 629-20-9; styrene, 100-42-5; 1,1-diphenylethylene, 530-48-3; tetramethylallene, 1000-87-9;

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1,1-dicyclopropylethylene, 822-93-5; *tert*-butylethylene, 558-37-2; cyclohexene, 110-83-8; cyclooctene, 931-88-4; norbornene, 498-66-8; vinyl acetate, 108-05-4; 2,2-dimethyl-3-(trimethylsiloxy)-3-butene, 17510-46-2; 1-phenyl-1-(trimethylsiloxy)ethylene, 13735-81-4; *p*-benzoquinone, 106-51-4; 2-(3-methyl-2-butenyl)-*p*-benzoquinone, 5594-02-5; 7-phenylbicyclo[4.2.0]-3-octene-2,5-dione, 70681-10-6; 2,6-dimethyl-*p*-benzoquinone, 527-61-7; 3',3'-diphenylspiro[2,5-cyclohexadien-1,1'-[2]oxacyclobutan]-4-one, 81741-26-6; (1'α,2'β,5'β,6'α)-spiro[2,5-cyclohexadiene-1,4'-[3]oxatricyclo[4.2.1.0^{2,5}]nonan]-4-one, 72283-21-7; 3-methyl-2-butenyl-*p*-benzoquinone, 81741-27-7; 2-methyl-3-(2-hydroxyethyl)-1,4-dimethoxynaphthalene, 51794-09-3; 2-methyl-3-(2-hydroxyethyl)-1,4-naphthoquinone, 76670-45-6; methyl lapachol, 17241-45-1.

Mild and Simple Biomimetic Conversion of Amines to Carbonyl Compounds

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Abstract: 4-Formyl-1-methylpyridinium benzenesulfonate is a convenient reagent for the chemical modification of primary amines to aldehydes and ketones. This method mimics the biological process for transamination reactions with pyridoxal (vitamin B_6). As in that process, it involves imine formation, prototropic rearrangement, and hydrolysis. The conditions are extremely mild and are compatible with a large variety of sensitive functional groups. This process provides a simple and efficient alternative to the somewhat harsher procedures generally employed for such transformations.

Methods for the preparation of aldehydes and ketones are of constant interest, as evidenced by the vast body of accumulated literature on this subject. Typically, oxidations of primary and secondary alcohols and controlled reduction of certain carboxylate moieties most commonly afford the desired carbonyl compounds. The transformation of primary amines to carbonyl compounds has also received considerable attention. A variety of metal oxidizing reagents have been used, including $KMnO_4$,[1] K_2FeO_4,[2] $Pb(OAc)_4$,[3] and NiO_2,[4] with varying results. The photolytic intermediacy of benzophenone[5] has also been investigated for the conversion of some simple primary amines to carbonyls. However, hydrolysis of the resulting imines affords a 50% yield of ketone, at best, necessitating the recovery of amine educt. The utility of chloramine intermediates[6] and dehydrogeneration with selenium reagents or via sulfinamides has also been demonstrated,[7] although formation of these imines and their hydrolysis often require elevated temperatures and strong acid.

A variety of transaminations have been developed that involve prototropic rearrangement and equilibration of Schiff-base intermediates to avoid these direct amine oxidations. The utility of the Sommelet reaction[8] suffers seriously from the hydrolytic conditions generally employed, and yields are frequently unacceptable for preparative purposes. Various nitroaryl aldehydes[9] have been used to study the position of Schiff-base equilibrium, and subsequent reactions afforded carbonyl compounds with generally poor results. Imines prepared from 3,5-di-*tert*-butyl-1,2-benzoquinone have been utilized[10] to afford ketones in high yield, although this method is not applicable to the preparation of aldehydes. Some complex heterocyclic systems[11,12] have been employed and in special cases are effective transaminating reagents. However, they involve multiple steps, and their utility has not been generally demonstrated.

One recent example of the prototropic rearrangement method involves the formation of imines with pyridine-2-carboxaldehyde.[13] Deprotonation with lithium diisopropylamide afforded the resonance-stabilized anion, which was subsequently protonated and hydrolyzed, affording some simple aldehydes and ketones in high yields. The chief disadvantage of this process lies in the strong base required and its potential incompatibility with functional groups in more complex substrates. Although this method was described as a biomimetic approach to the oxidative deamination of primary amines, a more precise modeling of the biological process might afford milder reaction conditions and therefore be compatible with a wide variety of functional groups.

The role of pyridoxal phosphate (**1**, vitamin B_6) in biological transamination sequences is well established.[14] This cofactor is exceptionally receptive to nucleophilic addition because of its highly polarized carbonyl group and therefore readily converts primary amines to their corresponding imines (Scheme I). The enzyme system responsible for the efficiency of this overall process serves two fundamental functions: (1) controlled protonation of the pyridine nitrogen and (2) subsequent abstraction of an imine hydrogen, initiating prototropic rearrangement of the original Schiff base. We projected that a quaternized pyridine-4-carboxaldehyde might suitably mimic the biological system when applied to the in vitro preparation of some functionalized aldehydes and ketones. Such a system has been developed and is presented in this report.

Results and Discussion

Our purpose was to develop a simple, mild, efficient, and versatile conversion of primary amines to aldehydes and ketones via a route that in principle mimics the pyridoxal–pyridoxamine (**1–2**, Scheme I) interconversion. In addition, we sought a convenient method for product isolation that would not require formation of related derivatives or chromatographic separations. The use of water-soluble pyridinium salts would thus afford clean separation of carbonyl products from all starting materials and intermediates. First, some simple transamination reactions were examined with 4-formyl-1-methylpyridinium iodide[15] (**3**). The

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