

Photosensitized Oxygenation of Benzyl Ethyl Sulfide

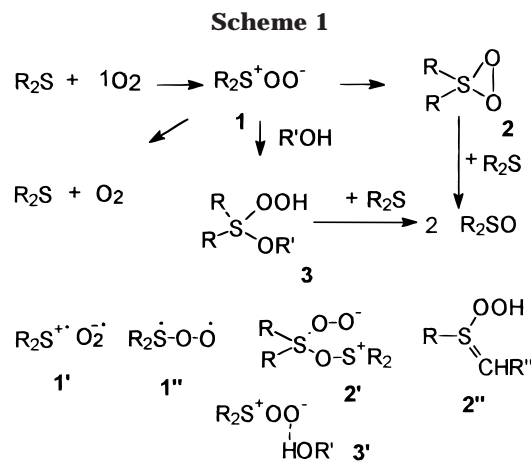
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Singlet oxygen adds to benzyl ethyl sulfide (**5**, total quenching rate ca. $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, little dependent on the solvent) to ultimately give benzaldehyde (**6**) and a small amount of the sulfone (**8**) in aprotic media (rate of the chemical reaction in benzene $5.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and mainly the sulfoxide (**7**) in protic media ($1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in methanol). In the presence of small amounts (0.002–0.3 M) of protic additives (alcohols, phenol, carboxylic acids), the sulfoxide becomes the main product in benzene also. Various evidence support the formation of two intermediates in aprotic solvents. The first one is an exciplex or a syn persulfoxide. It undergoes intramolecular hydrogen abstraction to give a ylide and finally benzaldehyde. Such rearrangement is either a concerted or a radicalic process and not a proton transfer (as indicated by the deuterium effect observed with the α -*d* benzyl sulfide and the occurrence of the process with the *p*-nitro and *p*-methoxy derivatives, **5'** and **5''**). This intermediate is not quenched except under relatively strong acidic conditions. A second intermediate, arising either from the first one or through a parallel path, has the properties usually associated with the persulfoxide (possibly it is the *anti* rotamer). This species gives some sulfoxide but mainly decays to the unreacted sulfide; it can be trapped intermolecularly, however, both by acids and by diphenyl sulfoxide (in the latter case it gives more of sulfone **8** than of sulfoxide **7**). The relative rates of protonation of both the first and the second intermediate (determined in benzene doped with protic additives) correlate with the gas-phase acidity of such additives. As for the reaction in neat alcohols and in benzene doped with acids, a single intermediate intervenes. This is better described as a *S*-hydroperoxy cation rather than a neutral hydroperoxysulfurane and is trapped by both diphenyl sulfoxide and sulfone at rates close to those measured for the photo-oxidation of diethyl sulfide.

Dialkyl- and aryl alkyl- (but not diaryl-) sulfides give the corresponding sulfoxides by reaction with singlet oxygen.^{1,2} This process has attracted considerable interest in view of its synthetic and biological implications. The course of the reaction depends on the medium.^{3–7} In aprotic solvents, oxygenation is inefficient, i.e., interac-



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(1) (a) Clennan, E. L. *Sulfur Rep.* **1996**, *19*, 171. (b) Ando, W.; Takada, T. In *Singlet O₂*; Frimer, A. A., Ed.; CRC: Boca Raton, 1985; Vol. 3, p 1. (c) Ando, W. *Sulfur Rep.* **1981**, *1*, 143. Foote, C. S. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 139. (d) Gorman, A. A. *Adv. Photochem.* **1992**, *17*, 217. (e) Jensen, F. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 4, p 49. (f) Bellus, D. *Adv. Photochem.* **1979**, *11*, 105.

(2) (a) Schenk, G. O.; Krauch, C. H. *Angew. Chem.* **1962**, *74*, 510. (b) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795. (c) Foote, C. S.; Denny, R. W.; Weaver, L.; Chang, Y.; Peters, J. W. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 139. (d) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191. (e) Wasserman, H. H.; Strehlow, W. *Tetrahedron Lett.* **1970**, 795. (f) Murray, R. W.; Jindal, S. L. *Photochem. Photobiol.* **1972**, *16*, 147. (g) Casagrande, M.; Gennari, G.; Cauzzo, G. *Gazz. Chim. Ital.* **1974**, *104*, 1251. (h) Monroe, B. M. *Photochem. Photobiol.* **1979**, *29*, 761. (i) Martin, C. D.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3511. (j) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947. (k) Gu, C. L.; Foote, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 49. (l) Clennan, E. L.; Oolman, K. A.; Yang, K.; Wang, D. X. *J. Am. Chem. Soc.* **1992**, *114*, 3021.

(3) Liang, J. J.; Gu, C. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717.

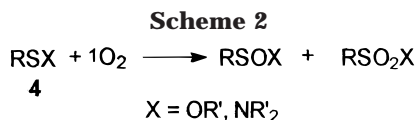
(4) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 1478.

(5) Akasaka, T.; Kako, M.; Sonobe, H.; Ando, W. *J. Am. Chem. Soc.* **1988**, *110*, 494.

(6) Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2677.

tion with singlet oxygen mainly (>95%) leads to physical quenching, although efficiency increases at low temperature. Two discrete intermediates are involved under this condition (Scheme 1). The first one has electrophilic character and is quenched, e.g., by diphenyl sulfoxide, and the latter one has nucleophilic character and is quenched by diphenyl sulfide. In methanol, on the contrary, chemical reaction predominates over physical quenching and a single intermediate (quenched by both Ph₂S and Ph₂SO) is involved. In Scheme 1, the intermediates have been identified as the persulfoxide **1**, the

(7) (a) Jensen, F. *J. Org. Chem.* **1992**, *57*, 6478. (b) Jensen, F.; Greer, A.; Clennan, E. L. *J. Am. Chem. Soc.* **1998**, *120*, 4439.



thiadioxirane **2** for aprotic media, and the adduct **3** for the reaction in methanol. Several pieces of evidence support this suggestion. However, other structures can be (and have been) considered: a tight ion pair (**1'**) or a diradical (**1''**) rather than zwitterion **1**; a sulfoxide-bound persulfoxide (**2'**) or, very recently, a ylide (**2''**) rather than heterocycle **2**; or a hydrogen-bonded persulfoxide (**3'**) rather than the alkoxy adduct **3** (see Scheme 1, lower part). Furthermore, the possibility that intermediates **1** and **2** are formed through parallel rather than sequential paths has been envisaged.⁶ Direct identification has not been possible except for a matrix isolation study,⁸ and evidence for such structures has been sought through the study of temperature, solvent, and substituent effect on the singlet oxygen reaction (in the last case using aryl alkyl sulfides),³⁻⁷ as well as through computational studies.^{4,6,7} A general consensus on the details of the mechanism seems not to have been reached as yet, however.

As mentioned above, chemical reaction accounts for only a small portion of the reaction of singlet oxygen with sulfides in aprotic solvents. This leaves little room for mechanistic studies under such conditions. Recently it has been found that with sulfenates⁹ and sulfenamides¹⁰ (**4**, Scheme 2) chemical reaction better competes with physical quenching, and this has allowed a detailed study. However, with such substrates heteroatom substitution directly at the sulfur atom considerably alters the electronic structure of the substrate and thus makes extension of the conclusions to sulfides not straightforward.

There is a class of sulfides which undergo a different chemical reaction with ¹O₂, the benzyl sulfides. Twenty years ago, Corey and Ouannès oxygenated some benzyl sulfides and found that benzaldehyde was produced.¹¹ This was rationalized as evidence in favor of the persulfoxide **1**. Partially related reactions of fluorenyl sulfides and thiazolidines¹² have been investigated, and further, it has been found that co-oxidation of olefins take place with such substrates. However, mechanistic data on the oxidation of benzyl sulfides are limited.¹³ We thought that a further investigation would be worthwhile; with these substrates, the initial interaction with singlet oxygen must be the same as with dialkyl sulfides, because there is little difference in the electronic structure. Thus, any change in the following chemical path may reveal the chemical nature of the intermediate(s), and the information obtained should be relevant for the general mechanism of sulfide photo-oxygenation.

Results

Main Features of Benzyl Ethyl Sulfide Photo-Oxygenation. Visible light irradiation of 0.01–0.1 M

(8) Akasaka, T.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 8085.

(9) Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1994**, *116*, 809. Clennan, E. L.; Chen, M. F. *J. Org. Chem.* **1995**, *60*, 6444.

(10) Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1995**, *117*, 4218.

(11) Corey, E. J.; Ouannès, C. *Tetrahedron Lett.* **1976**, 4263.

(12) Ando, W.; Nagashima, T.; Saito, K.; Kohmoto, S. *J. Chem. Soc., Chem. Commun.* **1979**, 154.

(13) Akasaka, T.; Sakurai, A.; Ando, W. *J. Am. Chem. Soc.* **1991**, *113*, 2696.

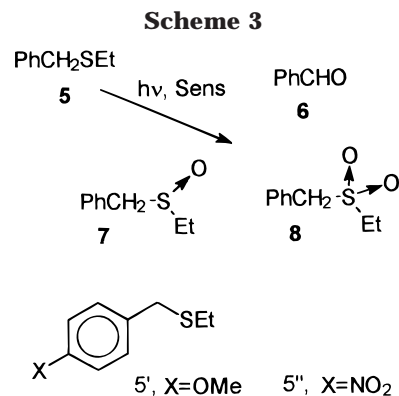


Table 1. Sensitized Photo-Oxygenation of Benzyl Ethyl Sulfide (5)

solvent	product distribution ^a			k_T (M ⁻¹ s ⁻¹) ^b	k_f (M ⁻¹ s ⁻¹) ^c
	6	7	8		
benzene	89	1	10	1.14×10^7	0.55×10^7
acetonitrile	90	3	7	1.22	0.61
methanol	25	63	12	0.94	1.2
benzene, MeOH 0.37 M	57	38	5		0.71

^a As determined at low (<20%) substrate conversion. ^b Reaction rate with singlet oxygen as determined by laser flash photolysis through the quenching of the 1270 nm emission. ^c Rate of the chemical reaction of **5** as measured in competition experiments in the presence of octaline.

solutions of benzyl ethyl sulfide (**5**) in benzene in the presence of tetraphenylporphine (TPP) gave benzaldehyde (**6**) as the major product (Scheme 3, Table 1), in accord with the report by Corey and Ouannès.¹¹ The aldehyde could be obtained in a ca. 80% yield by distillation at the end of the reaction. Minor products were sulfoxide **7** and sulfone **8**. Similar irradiation using Rose Bengal (RB) as the sensitizer in acetonitrile also gave mainly benzaldehyde. On the other hand, RB sensitized photo-oxygenation in methanol, ethanol, *tert*-butyl alcohol, or trifluoroethanol gave the sulfoxide accompanied by a lesser amount of benzaldehyde (Table 1). In all cases, the oxygenation was quenched by DABCO, as previously observed for dialkyl sulfides.^{2c}

Photo-Oxidation in Methanol. As it appears from the foregoing, the photo-oxygenation of benzylsulfide followed two different paths, either S-oxidation or C–S bond oxidative cleavage. The competition between the two processes depended on the medium. To obtain mechanistic information, the oxidation of **5** was examined in more detail. All experiments for this purpose were carried out at low conversion (<20%) to minimize secondary photoreactions.

As mentioned above, the major product from **5** in methanol was sulfoxide **7**. It has been demonstrated by Foote³ that sensitized irradiation of diethyl sulfide in the presence of both diphenyl sulfide and diphenyl sulfoxide causes co-oxygenation of such substrates, although these are both unreactive when irradiated in the absence of Et₂S. We thus carried out RB-sensitized oxidation of various **5**/Ph₂S mixtures and observed oxidation of both substrates to the corresponding sulfoxides. The ratio [7]/[Ph₂SO] obtained depended on the concentration of both sulfides. Foote's kinetic treatment was used; a plot of the [7]/[Ph₂SO] ratio vs [Ph₂S]⁻¹ at various concentrations of **5** is shown in Figure 1. Likewise, Ph₂SO was co-oxidized to diphenyl sulfone, with the product distribu-

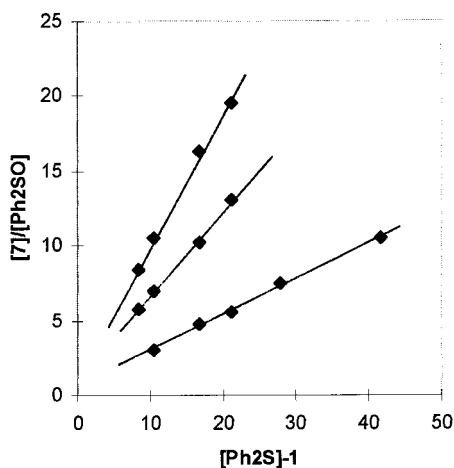


Figure 1. Ph₂S trapping of the PhCH₂SEt (**5**) photo-oxidation intermediate as a function of both concentrations in MeOH; slope = 0.238, 0.56, and 0.87 for 0.02, 0.052, and 0.082 M **5**, respectively.

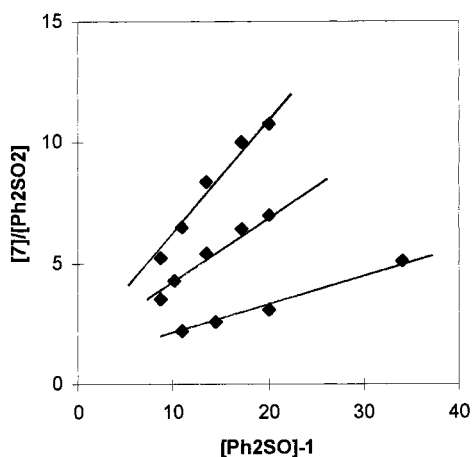


Figure 2. Ph₂SO trapping of the PhCH₂SEt (**5**) photo-oxidation intermediate as a function of both concentrations in MeOH; slope = 0.128, 0.299, and 0.502 for 0.02, 0.052, and 0.082 M **5**, respectively.

tion depending on the starting concentration of both substrates (see the $[7]/[\text{Ph}_2\text{SO}_2]$ vs $[\text{Ph}_2\text{SO}]^{-1}$ plot in Figure 2).

Photo-Oxidation in Benzene. Under this condition, the major product was benzaldehyde. One of the minor products, sulfone **8**, was present from the start and was formed at a constant rate throughout the process. On the contrary, practically no sulfoxide (**7**) was formed at low conversion. The amount of this compound became significant as long as the reaction proceeded, although it remained a minor product under this condition (9% at complete conversion of **5**). Addition of Ph₂S up to 0.5 M caused neither co-oxidation of the additive nor a change in the yield of the products arising from **5**. On the other hand, Ph₂SO was co-oxidized when added to **5**; in the presence of this additive, the yield of benzaldehyde remained constant, some sulfoxide **7** was formed, and the yield of sulfone **8** grew conspicuously. The extent to which the co-oxidation occurred did not depend on the concentration of sulfide **5**, as shown in Figure 3 (again, this held for low-conversion experiments). Likewise, the ratio $[8]/[\text{Ph}_2\text{SO}_2]$ was not a function of $[\mathbf{5}]$ although it depended on $[\text{Ph}_2\text{SO}]$. A plot of this ratio vs $[\text{Ph}_2\text{SO}]^{-1}$ is shown in Figure 4. Photo-oxygenation of a mixture of **5**

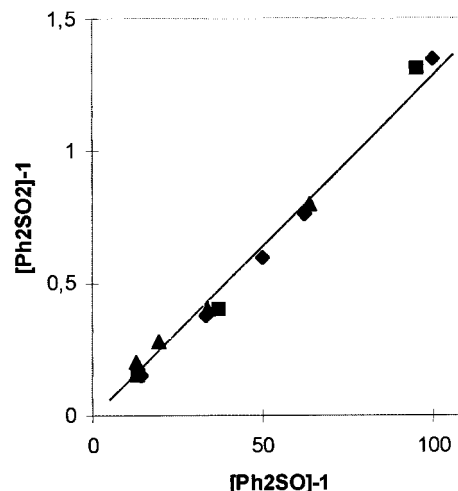


Figure 3. Co-oxidation of Ph₂SO in the presence of **5** as a function of both concentrations in benzene: (♦) 0.02 M **5**, (■) 0.05 M **5**, and (▲) 0.1 M **5**.

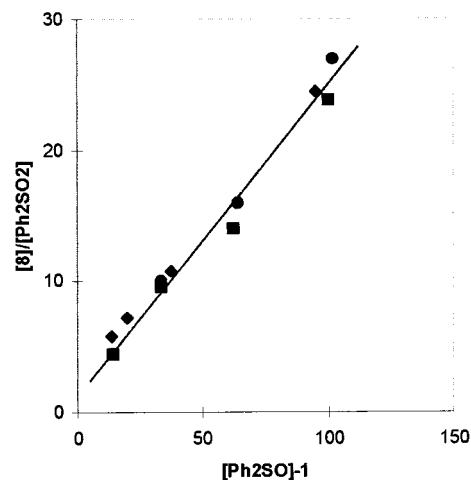


Figure 4. Ph₂SO trapping of the PhCH₂SEt (**5**) photo-oxidation intermediate as a function of both concentrations in benzene: (♦) slope = 0.22, 0.02 M **5**; (■) slope = 0.23, 0.05 M **5**; (●) slope = 0.25, 0.1 M.

and diethyl sulfide (both 0.05 M) in benzene caused an increase in the oxidation of the latter substrate to Et₂SO by a factor of 2.3 (with respect to the yield in the absence of **5**) and slowed down the oxidation of the former with no change in the product distribution.

Photo-Oxidation in Benzene Doped with Protic Additives. As shown above, the change from benzene to methanol brought about a complete change in the type of oxidative process occurring with benzyl ethyl sulfide. Recent experiments by Clennan¹⁴ showed that it is sufficient to add a few percent of methanol or of other alcohols to make efficient the sluggish photo-oxidation of diethyl sulfide in neat benzene. We looked at whether a low percentage of alcohols could affect the oxidation of **5** in terms of efficiency or of product distribution. When the photo-oxidation was carried out in benzene containing some methanol, the yield of sulfoxide increased somewhat with additions in the range of 0.37–1.85 M. *tert*-Butanol had little effect up to 1.5 M (although the reaction in neat *t*-BuOH gave **7** as the main product). Addition of trifluoroethanol was more effective, and the yield of sulfoxide

(14) Clennan, E. L.; Greer, A. *J. Org. Chem.* **1996**, *61*, 4793.

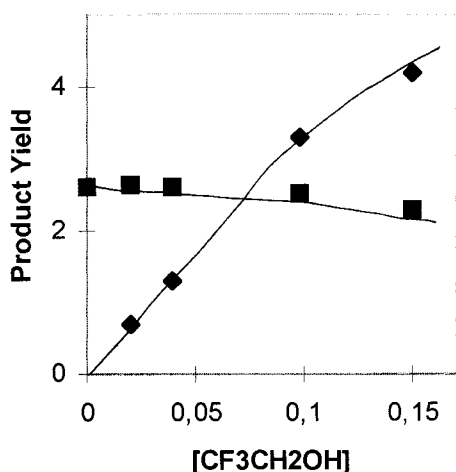


Figure 5. Yield of the photo-oxidation products from **5** (0.05 M) in benzene as a function of the concentration of added trifluoroethanol: (■) benzaldehyde (**6**), (◆) sulfoxide (**7**).

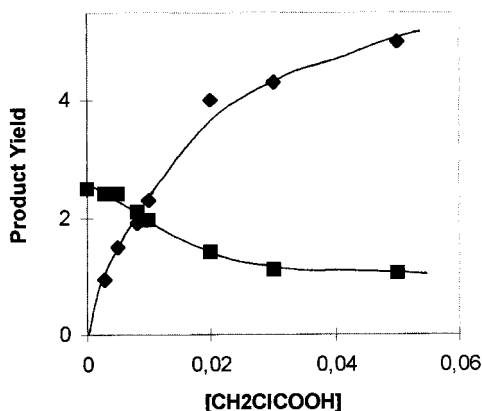


Figure 6. Yield of the photo-oxidation products from **5** (0.05 M) in benzene as a function of the concentration of added chloroacetic acid: (■) benzaldehyde (**6**), (◆) sulfoxide (**7**).

already increased significantly at 0.02 M concentration; this became the major product at 0.1 M (Figure 5). We pursued the examination with other protic additives, viz. *m*-nitrophenol, acetic acid, and chloroacetic acid. In these cases, an even smaller addition was sufficient to obtain a significant increase in the sulfoxide yield (e.g., with as low as 0.002 M chloroacetic acid), and furthermore, a drop in the benzaldehyde yield was observed, although this effect was much less apparent (see Figure 6 for the case of $\text{CH}_2\text{ClCO}_2\text{H}$).

Rate of the Photo-Oxidation. The rate of the reaction of **5** with singlet oxygen (k_T) was determined by quenching of the 1270 nm emission and was found to be little affected by the nature of the solvent (Table 1). The rate of chemical reaction of this sulfide (k_r) was then measured in competition experiments with octahydronaphthalene (supposed, as usual, to be photo-oxidized at a solvent-independent rate), following the method used by Foote.¹⁵ The data in Table 2 show that sulfide **5** was oxidized more efficiently in methanol than in benzene, although the increase was only by a factor of 2, not >20 as observed with diethyl sulfide.

Substituent Effect. The effect of a *para* substituent on the reaction was tested. It turned out that both

Table 2. TPP-Sensitized Oxygenation of *para* Substituted Benzyl Ethyl Sulfides^a

substituent	product distribution			k_T ($\text{M}^{-1} \text{s}^{-1}$)	k_r ($\text{M}^{-1} \text{s}^{-1}$)
	6	7	8		
4-OMe	82	8	5	1.66×10^7	0.52×10^7
4-NO ₂	70	5		0.17	0.10

^a Data obtained as in Table 1.

Table 3. Deuteration Experiments

substrate	conditions	PhCDO/PhCHO ^a
PhCHDSEt	benzene, TPP	3.63
PhCHDSEt	acetonitrile	2.95
PhCHDSEt	methanol	2.70
PhCH ₂ SEt	methanol <i>O-d</i>	0

^a In all cases there was no measurable (gas/mass experiments) change in the H/D ratio in either unreacted **5**, sulfoxide **7**, or sulfone **8**.

4-methoxy- and 4-nitrobenzyl ethyl sulfides (**5'** and **5''** in Scheme 3) gave the corresponding benzaldehydes by TPP-sensitized oxygenation in benzene. Both the rate of total quenching (k_T) and the rate for chemical reaction (k_r) were affected by the substituent, with a somewhat lower effect in the latter case (Table 2).

Deuterium Labeling. The photo-oxidation was similarly carried out using **5- α -d**. The D/H content in the benzaldehyde (**6**) formed under this condition was >1, as determined by GC/MS experiments. The results are reported in Table 3. On the other hand, the D/H ratio was unitary (in the limits of the experiment) in sulfone **7** and sulfoxide **8**. Furthermore, no deuterium incorporation was measured in the recovered starting material or in any of the products when the photooxidation of **5** was carried out in methanol *O-d*.

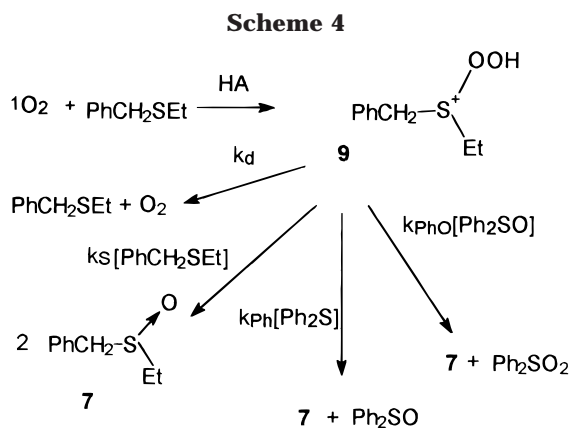
Discussion

Comparison with the thoroughly investigated photo-oxygenation of diethyl sulfide^{1,3,6,14} will show in which respect the benzyl sulfide (**5**) oxygenation is different and thus where a new mechanistic insight can come from. All of the observed reactions are quenched by DABCO, just as with dialkyl sulfides,^{2c} and involve singlet oxygen. The rate constant of singlet oxygen quenching by **5** ($k_T = 1.14 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in benzene, see Table 1) is on the same order as that obtained with Et_2S (reported as 1.71, 2, or $3.04 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)^{10,14,16} but somewhat lower, a fact that may be related to a slight steric hindering, as it is known that this factor has a strong effect with more bulky sulfides.^{2h} This rate depends neither on the polarity nor on the proticity of the medium (within 20%), as it is most often the case for singlet oxygen reactions and has been proved by Clennan for the case of alkyl sulfides.^{10,14} Electronic effects are significant, as shown by the 50% increase of k_T in the 4-methoxy substituted derivative **5'** (though, as expected, the effect is smaller than with thioanisole, where a 4-OMe group increases k_T by a factor of 3)^{2h} and the considerable drop of k_T in the 4-nitro derivative **5''**.

Summing up, the initial interaction of singlet oxygen with **5** does not differ from the case of dialkyl sulfides.

(15) Higgins, R.; Foote, C. S.; Cheng, H. *Adv. Chem. Ser.* **1968**, *77*, 102.

(16) (a) Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765. (b) Wilkinson, F. In *Singlet Oxygen. Reaction with Organic Compounds and Polymers*; Ranby, B., Rabek, J. F., Eds.; Wiley: London, 1978; p 27.



However, this substrate is better suited for mechanistic studies because the chemical reaction remains efficient in aprotic media and product distribution is a sensitive function of the medium characteristics (see e.g., Table 1 and Figures 5 and 6), whereas with dialkyl sulfides, a single product, the sulfoxide, is obtained, efficiently in alcohols and inefficiently in aprotic solvents. With **5**, cleavage of the C–S bond is dominant in aprotic solvents and S-oxidation is dominant in protic solvents. It is sufficient to add a small amount of a protic additive to make S-oxidation occur also in a benzene solution (e.g., as low as 0.002 M with $\text{CH}_2\text{ClCO}_2\text{H}$). The most effective among such additives also depress the yield of benzaldehyde, but this requires a larger addition than for producing the sulfoxide form. Another characteristic is that, in methanol, **5** co-oxidizes both Ph_2S (an electrophilic acceptor) and Ph_2SO (a nucleophilic acceptor), just as it occurs with Et_2S , whereas in benzene, only the latter additive is co-oxidized (and furthermore appears to catalyze the oxidation of **5** to the sulfone). Clearly, a variety of intermediates are involved. In the following, we show that the previously proposed mechanism can be conveniently adapted for accommodating the present data in an economic way, and a new insight into the nature of the intermediates is obtained.

The Oxidation in Protic Media. We begin with the oxidation in methanol. Under this condition, the photo-oxidation of **5** closely follows the well-known pattern of other alkyl sulfides. Both Ph_2S and Ph_2SO are co-oxidized under this condition, and the co-oxidation yield depends on the concentration of **5**, showing that both of these additives compete with benzyl sulfide for the same intermediate. Thus, the single-intermediate mechanism demonstrated by Foote for Et_2S operates also with **5**, as shown in Scheme 4.³ In this scheme, the quenched intermediate is indicated as the protonated persulfoxide, viz., the S-hydroperoxy cation **9**, rather than a methanol adduct such as **3** (compare Scheme 1). This is because it is the acidity of the medium, not its nucleophilicity, which determines the course of the reaction, as will be discussed later in more detail.

If Scheme 4 holds, steady state eqs 1 and 2 can be derived and are valid for low-conversion experiments, where secondary oxygenation reactions are unimportant (compare ref 3).

$$\frac{[7]}{[\text{Ph}_2\text{SO}]} = 1 + \frac{2k_{\text{SO}} [\text{5}]}{k_{\text{Ph}} [\text{Ph}_2\text{S}]} \quad (1)$$

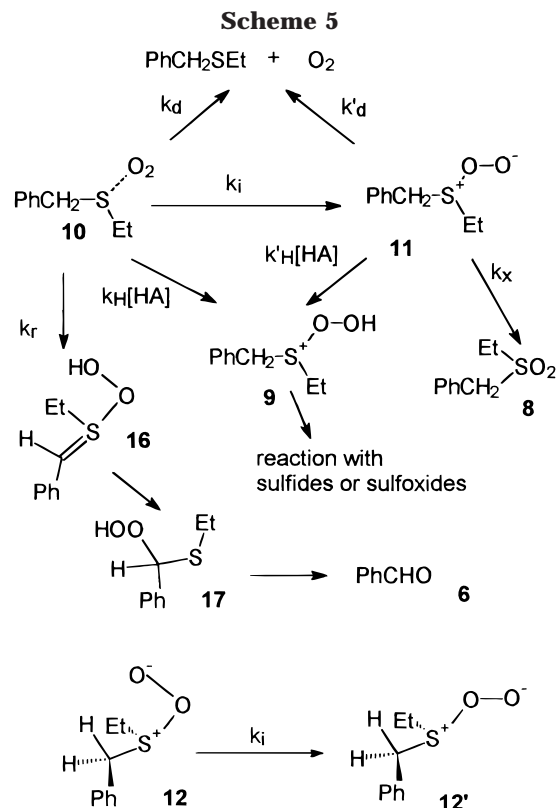
$$\frac{[7]}{[\text{Ph}_2\text{SO}_2]} = 1 + \frac{2k_{\text{SO}} [\text{5}]}{k_{\text{PhO}} [\text{Ph}_2\text{SO}]} \quad (2)$$

Figures 1 and 2 show that the expected linear dependence of the ratios $[7]/[\text{Ph}_2\text{SO}]$ and $[7]/[\text{Ph}_2\text{SO}_2]$, respectively, on the reciprocal of the additive is followed. As expected, the observed correlations depend on the concentration of **5** and have a common intercept. Plots of the data at three different concentrations are shown in Figures 1 and 2. These provide the ratios $k_{\text{SO}}/k_{\text{Ph}}$ (5.0) and $k_{\text{SO}}/k_{\text{PhO}}$ (3.0), respectively. These values are only slightly larger than those obtained with diethyl sulfide (respectively, 4.0 and 2.77).³ Thus, the intermediate formed from **5** in protic solvents has the same structure and the same reactivity as that formed from other dialkyl sulfides.

Intermediates in Aprotic Media. Foote demonstrated that, in contrast to the methanol case, the intervention of two intermediates is required for rationalizing the photo-oxygenation of diethyl sulfide in benzene (Scheme 1).³ These were identified as the nucleophilic persulfoxide **1** and the electrophilic thiadioxirane **2**. With **5**, co-oxidation of Ph_2SO but not of Ph_2S is observed. Furthermore, the experiments in benzene doped with protic additives (Figure 5, Table 1) show that an intermediate is intercepted and diverted to give the sulfoxide **7** under low acidity conditions. It is reasonable that both electrophiles, the proton and Ph_2SO , trap the same intermediate, i.e., the first one in Foote's scheme. Thus, the persulfoxide is also an intermediate in the oxygenation of **5**. However, under such conditions, benzaldehyde is still formed in about the same yield as in neat benzene, whereas its formation is quenched, with a further increase in the formation of the sulfoxide, under more acidic conditions (compare Figure 5, weak acid, with Figure 6, stronger acid), though not in the presence of Ph_2SO . This demands a further intermediate leading to benzaldehyde, which either is a precursor of the above one or is formed through a parallel independent path and which can be protonated as can the persulfoxide, though less efficiently.

There are two viable possibilities for this pair of intermediates. The first one is that one is a sulfide-oxygen exciplex (**10**, not an ion pair because dialkyl sulfides, including **5**, are not sufficiently good donors for reducing singlet oxygen) and the other one persulfoxide **11**. The intermediacy of an exciplex has been previously considered and fits well with the large increase of the rate of photo-oxygenation for dialkyl sulfides observed by lowering the temperature (although the total quenching rate of singlet oxygen does not change).^{1a,d,2k,l} Exciplex **10** (see Scheme 5) has no chemical path available with dialkyl sulfides and in that case simply decays to the components (k_d). With **5**, however, intramolecular hydrogen transfer from the activated benzylic position (k_i) occurs rather efficiently and ultimately gives benzaldehyde. Persulfoxide **11** may be formed from it by S–O bond formation (k_f).

An alternative rationalization for the two intermediates would be a conformational equilibrium of the persulfoxide. Calculations by Jensen and Foote¹⁷ and by Jensen^{7a} on the singlet oxygen/dimethyl sulfide addition showed that the first intermediate is the persulfoxide with C_s symmetry and the oxygen–oxygen bond bisecting



the Me-S-Me angle. However, a C_1 rotational (by 120°) isomer of the persulfide was also located as a minimum and was only slightly more energetic (1.2 kcal/mol). Clennan has suggested that activation by alcohols involves concomitant rotation and complexation of the persulfide.¹⁴ Thus, it may be that the syn persulfide (**12**), better suited for intramolecular hydrogen abstraction, is formed first and then rearranges to the *anti* rotamer **12'**, better suited for intermolecular reactions, e.g., protonation. In that case, formulae **12** and **12'** (bottom of Scheme 5) should be substituted for **10** and **11**, respectively, in the scheme, and k_i is the rotation rate. The role of these intermediates in the reactions occurring in benzene is discussed in the next sections.

Protonation of the Intermediates. We propose that both the first and the latter intermediates are protonated in the presence of protic additives (rates k_H and k'_H , respectively, see Scheme 5), giving the single intermediate characteristic of protic media (**9**, shown also in Scheme 4). This step is required in order to generate sulfoxide **7**, which is *not* formed by irradiation in neat benzene (at least at low conversion, see a further comment below). In our scheme, the yield of sulfoxide **7** depends on the concentration of the protic additives in a complex way, being the sum of two contributions (see eq 3, where m is the probability that the protonated intermediate **9** is finally converted into sulfoxide **7**).

$$[7] = \frac{mk_H[HA]}{k_r + k_i + k_d + k_H[HA]} + \frac{mk_i k'_H[HA]}{(k_r + k_i + k_d + k_H[HA])(k_x + k'_d + k'_H[HA])} \quad (3)$$

The rates of protonation for the two intermediates are largely different. Figure 5 shows that when using weak acids such as alcohols the yield of **7** increases until a

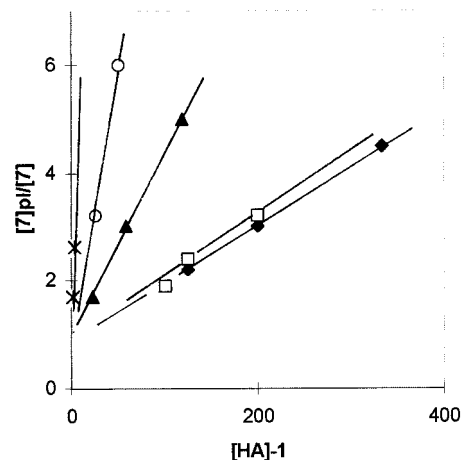


Figure 7. Acid quenching of the photo-oxidation of **5** (0.05 M) in benzene as observed on the formation of sulfoxide **7** and as a function of the additive concentration. For the sake of clarity, only some of the points are shown: (x) methanol, slope = 0.66; (o) trifluoroethanol, slope = 0.117; (\blacktriangle) acetic acid, slope = 0.0347; (\square) *m*-nitrophenol, slope = 0.0125; (\blacklozenge) chloroacetic acid, slope = 0.0111.

Table 4. Relative Rate of Protonation for Oxygenation Intermediates^a

	1st intermed, 10	2nd intermed, 11
methanol		1
trifluoroethanol	1	5.6
acetic acid	4.7	19.0
<i>m</i> -nitrophenol	27.5	52.8
chloroacetic acid	19.0	59.5

^a Slopes of the correlation lines in Figures 8 and 7, respectively.

plateau value, $[7]_{pl}$, is reached, with no significant reduction in the benzaldehyde yield. Thus, the second intermediate **11** is essentially completely protonated before protonation of the first-formed complex **10** occurs to a significant degree. Therefore, under such conditions, the yield of **7** is given by the second term of eq 3, and eq 4 holds. Furthermore, with stronger acids (carboxylic

$$\frac{[7]_{pl}}{[7]} = \frac{k_x + k'_d + k'_H[HA]}{k'_H[HA]} = 1 + \frac{k_x + k'_d}{k'_H[HA]} \quad (4)$$

acids or the nitrophenol) a sharp increase in the yield of **7** is obtained at a low concentration, where the yield of **5** undergoes only a marginal drop (see Figure 6 for the example of chloroacetic acid **9**). Therefore, eq 4 can also be used for analyzing the protonation of the second intermediate by strong acids, provided that the experiments at low concentration are considered.

Figure 7 shows that the linear plots expected from eq 4 are obtained for all the protic additives we used. With the reasonable assumption that unimolecular reactions of the intermediate are not affected by these small additions of protic agents, the slopes of such plots are proportional to the rates of protonation of persulfide **11** by such additives. These values are reported in Table 4, taking methanol as the reference.

On the other hand, at a higher acid concentration, the yield of benzaldehyde decreases and a further increase in the yield of sulfoxide **7** takes place. This effect is not observed with methanol (up to 1.8 M), barely detectable with trifluoroethanol, and clearly apparent with stronger acids (see e.g., Figure 6 for chloroacetic acid). Apparently,

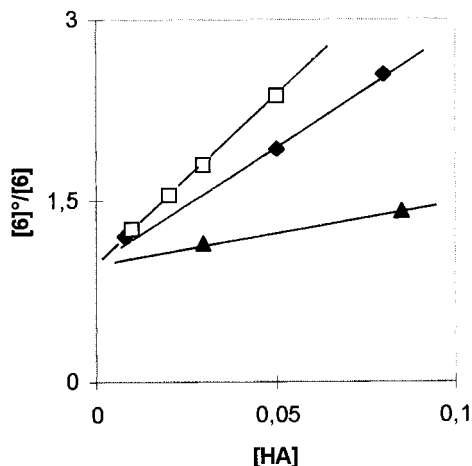


Figure 8. Acid quenching of the photo-oxidation of **5** (0.05 M) in benzene as observed on the formation of benzaldehyde (**6**) and as a function of the additive concentration. For the sake of clarity, only some of the points are shown: (▲) acetic acid, slope = 4.7; (□) *m*-nitrophenol, slope = 27.5; (◆) chloroacetic acid, slope = 18.6. Trifluoroethanol (not shown), slope = 1.

under this condition, the first intermediate **10** is in turn protonated. The yield of the sulfoxide now depends on two contributions, but monitoring the drop in the aldehyde yield allows evaluation of the protonation of the first intermediate alone. The ratio between the yield of the aldehyde in the absence ($[6]^0$) and in the presence of the acid is given by eq 5. Figure 8 shows the expected linear

$$\frac{[6]^0}{[6]} = \frac{k_r + k_i + k_d + k_H[HA]}{k_r + k_i + k_d} = 1 + \frac{k_H[HA]}{k_r + k_i + k_d} \quad (5)$$

dependence of such ratio on the concentration of the acid and allows the evaluation of the relative rate of protonation of the complex **10** (Table 4, relative to trifluoroethanol).

If quenching of the intermediates indeed involves protonation, a correlation of the observed effect with the strength of the acids is expected. Figure 9 shows the dependence of $\log k_H(\text{rel})$ (both series in Table 4) on the gas-phase acidities.¹⁸ This parameter is chosen because it is thought to better match the results in benzene than would the pK_a values in water or DMSO. In fact, this fits the data satisfactorily, e.g., *m*-nitrophenol causes a larger effect than acetic acid, corresponding to the acidity order in the gas phase, not in water. Such a dependence exists for the protonation of both **10** and **11** and is steeper in the former case. The rate of protonation increases over almost 2 orders of magnitude from methanol to chloroacetic acid. Less acidic alcohols, such as *tert*-butanol, cause practically no effect unless present in a massive amount.

We also studied the increased efficiency of the diethyl sulfide *S*-oxidation in benzene doped with the same additives and found that the protonation rate increases in an even more conspicuous way (by a factor of 450 from MeOH to $\text{CH}_2\text{ClCO}_2\text{H}$).¹⁹ Clennan had previously ob-

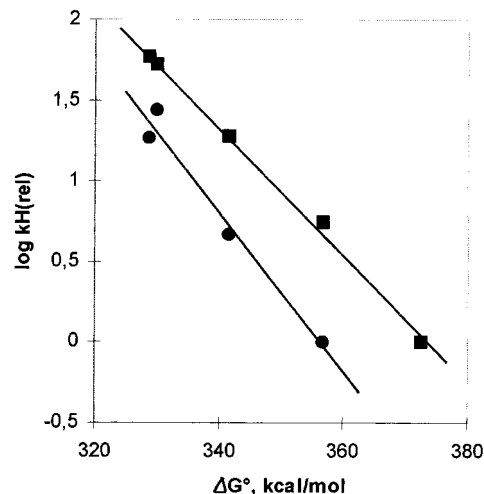
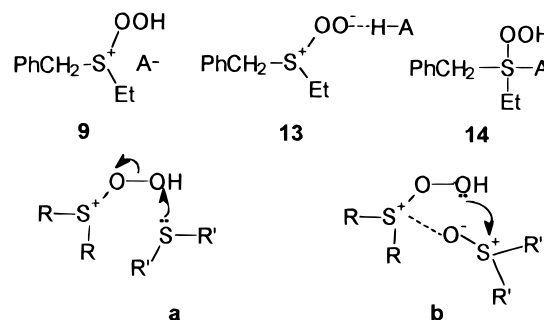


Figure 9. Dependence of the relative rate of protonation of the intermediates of the photo-oxidation of **5** in benzene (from Figure 8) as a function of the acidity of the additive in the gas phase: (●), first intermediate, **10**; (■), second intermediate, **11**.

Scheme 6



served a correlation of the diethyl sulfide photo-oxidation rate with the acidity of the additive in a study limited to alcohols and concluded that a concerted protonation–nucleophile addition to the persulfide took place to give **3** (Scheme 1).¹⁴ However, the present study shows that the correlation with acidity still holds with much stronger acids than the alcohols, and thus the determining factor must be the acidity and not the nucleophilicity of the additive.

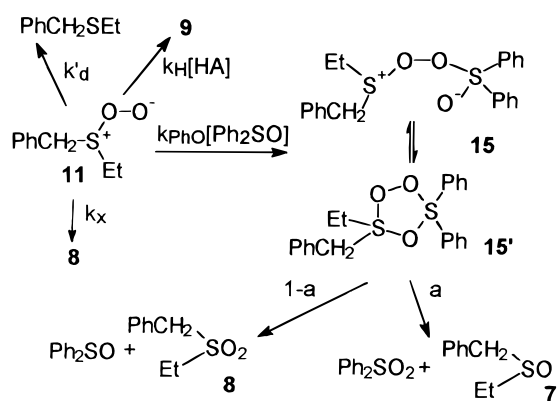
The fact that the rate of quenching depends on the acidity of quencher HA is per se no evidence about the structure of the resulting species, viz., the single intermediate characteristic of protic media. We indicated it as cation **9** in our schemes, but it may be a hydrogen-bonded complex (**13**, see Scheme 6) or an adduct (**14**≡**3** of Scheme 1 in the case of methanol). Recent calculations failed to locate **3** as a minimum,^{7b} and at any rate, if an adduct is involved, its chemistry is not influenced by group A (alkoxy, phenoxy, or carboxy). For the sake of simplicity, therefore, we referred to cation **9** in the present discussion. We notice that such species reasonably explain the observed oxidation of both sulfides (electrophilic OH transfer) and sulfoxides (because initial coulombic attraction between positively charged sulfur and the sulfoxide oxygen may facilitate ensuing nucleophilic OH transfer, see Scheme 6, reactions indicated as a and b) and is probably a better candidate than **14** (or **3** for Et_2S).

Trapping of the Intermediates by Electrophiles. The first intermediate (**10**) is protonated only under

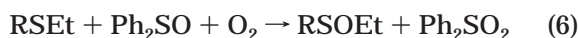
(18) Cummings, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1. (b) Batrness, J. E.; Scott, J. A.; McIver, R. T. *J. Am. Chem. Soc.* **1979**, *101*, 6056. (c) Fujio, M.; McIver, R. T.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017. (d) Fujio, M.; McIver, R. T.; Taft, R. W.; Bordwell, F. G.; Olmstead, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 2717.

(19) Unpublished data from the authors' laboratory.

Scheme 7



markedly acidic conditions since the competing unimolecular reaction (see further below) make its lifetime too short. Therefore, it does not react significantly with other electrophiles. The latter one (**11**), however, is trapped by diphenyl sulfone (Scheme 7). Kinetically, the observed trapping parallels that observed by Foote in the case of diethyl sulfide³ in the sense that quenching by Ph₂SO does not depend on the concentration of **5** (see Figure 3). However, the chemical reaction is different. In the case of diethyl sulfide, the persulfide rearranges to the thiadioxirane (**2** in Scheme 1 or ylide **2''** according to a recent computation)^{7b} and this gives diethyl sulfoxide by reaction with Et₂S or Ph₂S. Quenching of the persulfide by diphenyl sulfone also gives diethyl sulfoxide according to eq 6 (R = Et). On the other hand, in the



case of benzyl sulfide **5**, no sulfoxide is formed nor is there quenching by Ph₂S, and thus there is no rearrangement to a thiadioxirane (see a further comment below). Moreover, addition of Ph₂SO leads in part to the sulfoxide according to eq 6 (R = PhCH₂) and in part appears to catalyze formation of benzyl sulfone **8**, according to eq 7.



The simplest rationalization of this result is that this had to do with the adduct between persulfide and Ph₂SO (see Scheme 7). Ando demonstrated on the basis of O-tracing experiments that it has the zwitterionic open-chain structure corresponding to **15** for the oxidation of dimethyl sulfide in the presence of dimethyl sulfoxide.²⁰ In the present case, however, the steric effect by the benzyl group may favor a cyclic structure such as **15'** which partitions between two alternative cleavage modes. Path (a) gives **7** and Ph₂SO₂, and path (1-a) gives **8** and Ph₂SO (Scheme 7).

Because, as seen above, sulfoxide **7** is not formed in benzene in the absence of Ph₂SO, this compound arises only via eq 7. The amount obtained is the same as that of diphenyl sulfone and depends on the concentration of added Ph₂SO (see eqs 8 and 9). In our experiments, the yield of **7** is somewhat larger than that of Ph₂SO₂; presumably because of the formation of a little **7** from another path (see next section). Therefore, the existence of a correlation was tested with Ph₂SO₂, and the double

reciprocal plot in Figure 3 shows that the linear behavior predicted by eq 9 is followed.

$$[\mathbf{7}] = [\text{Ph}_2\text{SO}_2] = \frac{ak_{\text{PhO}}[\text{Ph}_2\text{SO}]}{k_{\text{PhO}}[\text{Ph}_2\text{SO}] + k_x + k'_d} \quad (8)$$

$$[\mathbf{7}]^{-1} = [\text{Ph}_2\text{SO}_2]^{-1} = \frac{1}{a} + \frac{k_x + k'_d}{ak_{\text{PhO}}[\text{Ph}_2\text{SO}]} \quad (9)$$

Benzyl sulfone **8**, on the other hand, is formed through two paths, both directly in neat benzene and via the Ph₂SO-catalyzed path (eq 10). The ratio **[8]**/[Ph₂SO₂] is expected to be unaffected by the concentration of **5** and to show a reciprocal dependence on [Ph₂SO], as indicated in eq 11. This is verified in Figure 4. According to eqs 9

$$[\mathbf{8}] = \frac{k_x + (1-a)k_{\text{PhO}}[\text{Ph}_2\text{SO}]}{k_{\text{PhO}}[\text{Ph}_2\text{SO}] + k_x + k'_d} \quad (10)$$

$$\frac{[\mathbf{8}]}{[\text{Ph}_2\text{SO}_2]} = \frac{k_x + (1-a)k_{\text{PhO}}[\text{Ph}_2\text{SO}]}{ak_{\text{PhO}}[\text{Ph}_2\text{SO}]} = \frac{1-a}{a} + \frac{k_x}{ak_{\text{PhO}}[\text{Ph}_2\text{SO}]} \quad (11)$$

and 11, the intercepts of the plots in Figures 3 and 4 allow evaluation of the partitioning from adduct **15'**, and the value of $a \approx 0.2$ results. From the slope of the line in Figure 4 and by taking $a = 0.2$, the ratio k_x/k_{PhO} is calculated as 0.046. This is twice as much as that determined by Foote for the analogous nucleophilic attack of Ph₂SO on the diethyl sulfide persulfide in benzene.³ The present evaluation should not be over-stressed because it involves approximations from two different measurements, but it is remarkable that the two evaluations are quite close. Thus, unimolecular reactions and reaction with Ph₂SO competes in the same way in the case of Et₂S⁺OO⁻ and in the case of the benzyl persulfide (or at least of the *anti* rotamer **12'** if such an equilibrium is involved), even if the chemical products are in part different.

C-S Bond Cleavage. C-S bond cleavage to give benzaldehyde is the main reaction in aprotic media and is reasonably formulated as involving intramolecular hydrogen transfer from the activated α position, as shown in Scheme 5. The intermediacy of a *S*-hydroperoxysulfonium ylide (**16** in the present case) has been initially proposed by Ando for the photo-oxygenation of thiazolidine and benzyl sulfides¹² and later shown to be the active species in the co-oxidation of alkenes observed in the presence of such sulfides¹³ and in the oxidation of thioanisole.²¹ This undergoes a Pummerer-type rearrangement to the α -hydroperoxysulfide **17** (Scheme 5), isolated in analogous cases,¹³ and then cleaves to the aldehyde.

Experimental support for the intermediacy of ylide **16** is offered by the secondary oxidation we observe. Ando has shown that such ylides (and not the quite stable hydroperoxide analogous to **17**) are oxidizing species. Thus, these epoxidize alkenes (although only when present in a large excess and high concentration, typically 7 M) and oxidize dimethyl sulfide.¹³ This explains why sulfoxide **7**, not a primary product and not detected at

(20) Akasaka, T.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1203.

(21) Ishiguro, K.; Hayashi, M.; Sawaki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7265.

the beginning of the reaction, is formed at a later stage of the reaction. This reasonably occurs by oxygen transfer from **16**, which accumulates to a certain extent, to **5**. Likewise, co-oxidation of equimolecular amounts of **5** and diethyl sulfide leads, as one may expect, to a decreased reaction of **5** (this is proportional to the part of singlet oxygen competitively quenched by Et₂S and involves no change in product distribution) but gives an enhanced yield of Et₂SO (2.3 times with respect to irradiation of Et₂S alone). Thus, here Et₂S is oxidized by ylide **16**.

As for the mechanism by which **16** is formed, very recent calculations by Jensen et al.^{7b} suggest that hydrogen transfer to give a ylide is a viable path from the persulfoxide in the case of dimethyl sulfide. However, the above kinetic analysis shows that benzaldehyde is formed from **5** via an intermediate which precedes the persulfoxide, or at least a second intermediate that has the chemical characteristics generally attributed to the persulfoxide. Thus, as shown in Scheme 5, the possibilities are either that the ylide is formed directly from complex **10** or that two persulfoxide conformations are formed sequentially and only for the first one is hydrogen transfer significant. Whichever is the exact mechanism, experimental evidence suggests that the O-H bond is formed to a considerable degree in the transition state, as shown by the marked selectivity in the case of α -*d* **5** (ratio 3.63 for PhCDO in benzene), and that the reaction is no proton transfer, because the rate of formation of the benzaldehyde (k_r) is not determined by charge stabilization (it remains the same with the 4-methoxy derivative of **5**, and although it decreases with the 4-nitro derivatives, the ratio k_r/k_T increases in that case, and the effect is small, see Table 1). Thus, a concerted or radical pathway is indicated. In the first case, the reaction would proceed via exciplex **10** and follow a concerted path analogous to the alkene ene addition, and in the latter, a diradicalic character of the first-formed persulfoxide **12** would be indicated²² (also notice that a little bibenzyl is formed during the photo-oxidation, again pointing to a radical course). Calculation on dimethyl sulfide did not support a concerted path,^{7b,21} but this may not be relevant because C-S bond cleavage occurs only with activated C-H, as with the present benzyl derivatives. Notice also that the intermediate is somewhat polarized, being quenched by acids, albeit only under relatively severe conditions.

Formation of Sulfoxide. Finally, some notes are in order with regard to the formation of sulfoxide **8**. Whether the intermediate leading to the sulfone is the same as that intercepted by sulfides has been the subject of some controversy.^{1,6} In particular, the work by Sawaki suggests that the thiadioxirane is formed competitively with, not sequentially to, the persulfoxide and then opens up to the sulfone.⁶ The unimolecular mechanism for the formation of the sulfone was supported by ¹⁸O₂ experiments. Sulfoxes are formed in high yield from Et₂S at low temperature in an apolar medium²³ and from disul-

fides.²⁴ Recent computational (on dimethyl sulfide)^{7b} and experimental (on thioanisole)²¹ evidence discard the intermediacy of a thiadioxirane and suggest that in apolar media the sulfone is formed via a hydroxypersulfonium ylide, so that formation of the sulfone or C-S bond cleavage depend on the partitioning of such an intermediate. As it appears from the previous section, ylide **16** is an intermediate for benzaldehyde formation in the present case and arises from the first intermediate, an exciplex or a diradicalic persulfoxide. One may consider whether sulfoxide may be formed through the same path or via the second intermediate. Contrary to the thioanisole case, the proportion of sulfoxide is low here and it is difficult to arrive at an unambiguous conclusion. However, the fact that acids quench the formation of sulfone **8** while promoting that of sulfoxide **7** and the form of the observed [8]/[Ph₂SO₂] vs [Ph₂SO] relation (Figure 4) suggest that **8** results from the latter one (k_x in Scheme 5), although it gives no indication of how such a conversion occurs. Certainly, there is no evidence for a thiadioxirane in this case, nor for any intermediate quenched by nucleophiles. As discussed in a previous section, an enhanced yield of **8** is obtained in the presence of Ph₂SO, apparently via an unprecedented, but not unreasonable, fragmentation of adduct **15'** (see Scheme 7). This path does not affect formation of benzaldehyde but rather avoids unproductive decay (k_d) of the second intermediate (persulfoxide **11** or **12'**) to the components.

Overall Mechanism. The photochemistry of benzyl sulfide **5** is more complex than that of dialkyl sulfides. The competition of various paths in aprotic solvents, with relatively low amounts of some of the products, introduces into some of the present evaluations a certain degree of uncertainty. However, this varied chemistry offers a wealth of indications and justifies choosing this model for better understanding the nature of the intermediates involved in the photo-oxygenation of sulfides. Many of these results are easily reconciled with the known scheme, but some revision is appropriate. Since the electronic structure of **5** is little different from that of other dialkyl sulfides, most indications (except of course those based on steric factors) should have a general bearing for sulfide oxygenation.

The most significant information from the present results concerns the very first step of chemical reaction and suggests that an exciplex (**10**) or a diradicalic syn persulfoxide (**12**) is formed before the "classical" persulfoxide or in parallel to it. Such an intermediate has no path for chemical reaction with dialkyl sulfides, but an activated α -hydrogen reveals its presence and makes the reaction efficient also in aprotic solvents. The chemical quantum yield for intramolecular hydrogen transfer is ca. 0.5 in benzene, and thus, if the intermediates are formed sequentially, $k_r \cong k_i$ (see Scheme 5) and if they are formed in parallel, their yield is about the same. Since $\Phi \ll 0.05$ with dialkyl sulfides, no hint can be obtained for the elusive first intermediate in that case.

The second intermediate has all the characteristics attributed to the persulfoxide in the previous work. Indeed, such a classical persulfoxide (**11** or, specifically, the anti rotamer **12'**) mainly decays to unreacted sulfide

(22) (a) The diradicalic character of 1,3-dipoles has been demonstrated in a number of cases; see, e.g., ref 22b. Notice also that the overall deuterium effect on a multistep reaction such as that leading to benzaldehyde does not necessarily represent that involved in the first step, as assumed in the present discussion for the sake of simplicity. Calculations by Jensen et al. show that a significant deuterium effect may also be involved in the second step, the shift of the OOH group; see ref 7b. (b) Hiberty, P. C. *Isr. J. Chem.* **1983**, *23*, 10.

(23) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.

(24) Clennan, E. L.; Zhang, H. *J. Org. Chem.* **1994**, *7952*. Clennan, E. L.; Wang, D.; Zhang, H.; Clifton, C. H. *Tetrahedron Lett.* **1994**, *35*, 4723.

independent of the presence of a benzylic hydrogen, as one would expect because here only polar (and not radical or concerted) chemical paths are available. This intermediate can be made to react efficiently by protonation or trapping by Ph_2SO according to the well-known general pattern^{1,3,10,25} (e.g., the ratio k_x/k_{PhO} is within a factor of 2 with Et_2S and with **5**). Indeed, both intermediates are protonated, though with different efficiency, and certainly not at a diffusion-controlled rate, consistent with the idea that charge localization is not too high and these transients are moderate bases (and nucleophiles). As an example, with the strongest acid we used, chloroacetic acid, the second intermediate is wholly protonated at ca. 0.02 M, and three-fourths of the first one is protonated at 0.1 M; furthermore, only the latter one is trapped by Ph_2SO .

In turn, the protonated intermediate behaves exactly as the corresponding transient from Et_2S , giving the sulfoxide and co-oxidizing both Ph_2S and Ph_2SO . However, we noticed that this chemistry occurs also in the presence of phenol and carboxylic acids, not only alcohols as previously known,¹⁴ and its occurrence is proportional to the acidity and not the nucleophilicity of the additive. The effect of tiny additions of acids may be useful for directing the reaction and further suggests that this intermediate is better represented as a cation (**9**) than as a neutral adduct. Further subtle, probably steric, effects influence the evolution of some intermediates and, e.g., make the formation of the sulfone in aprotic solvents more important for **5** than from Et_2S , both directly and in the presence of Ph_2SO . Formation of the sulfone seems not to involve the ylide, in contrast to what was recently found for dialkyl sulfides^{7b} and thioanisole.^{21,26}

Experimental Section

Materials. Spectroscopic grade solvents were used. Benzene and acetonitrile were distilled from calcium hydride before use. Benzyl ethyl sulfide (**5**) and the substituted derivatives **5'** and **5''** were prepared by the reported method.²⁷ α -*d* **5** was analogously prepared from α -*d* benzyl chloride,²⁸ and the

purity was checked by NMR and mass spectroscopy. The sulfoxide (**7**)²⁹ and the sulfone (**8**),³⁰ as well as the corresponding methoxy- and nitro-substituted derivatives, were prepared by literature methods. Diphenyl sulfoxide and diphenyl sulfone (commercial samples from Aldrich) were purified by chromatography and recrystallization of the central fraction. Rose Bengal, tetraphenylporphine, and octahydronaphthalene were commercial products (Aldrich).

Photochemical Reactions. Irradiations were carried out in rubber-stoppered Pyrex tubes while passing a stream of oxygen saturated with the solvent. Four phosphor-coated 15 W lamps (Applied Photophysics) emitting from 350 to 700 nm were used as the light source. The course of the reaction was followed by VPC and/or HPLC and all reactions were discontinued at <20% conversion. The reported data are the average of at least three measurements within 5%. In the experiments with octaline, the solution was treated with triphenylphosphine before analysis to reduce the hydroperoxide to the allylic alcohol and then analyzed as above.

Analytical Methods. Gas chromatographic determination were carried out by means of a Hewlett Packard mode 5890 with a Innovax column (30 m \times 0.25 mm, 0.5 mm film thickness) and He as the carrier gas. The injector pressure was constant (12 psi). The temperature program was 50–140 °C (5 °C/min), 140–250 °C/min, 7 min final time). For mass determinations, this was equipped with a model 5971 mass detector. Under this condition, PhCHO and PhCDO were completely separated.

Photophysical Measurements. Rate constants for the quenching of singlet oxygen were measured by laser pulse spectroscopy (Spectra Physics Nd:YAG laser) by measuring the emission lifetime at 1270 nm after oxygen sensitization by phenalene.³¹

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(27) Modena, G. *Gazz. Chim. Ital.* **1960**, *89*, 834.

(28) Meyerson, S.; Rylander, P. N.; Eliel, E. L.; McCollum, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 2606.

(29) Cerniani, A.; Modena, G.; Todesco, P. E. *Gazz. Chim. Ital.* **1960**, *90*, 3.

(30) Buechi, J.; Prost, M.; Eichenberger, H.; Lieberherr, R. *Helv. Chim. Acta* **1952**, *35*, 1527.

(31) Schmidt, R. *J. Photochem. Photobiol.*, **A** **1994**, *79*, 11.

(25) Adam, W.; Golsch, D.; Goerth, F. C. *Chem. Eur. J.* **1996**, *2*, 255.

(26) The mechanism of formation of sulfones has not been fully clarified even with dialkyl sulfides. As an example, at low temperature, the sulfoxide–sulfone ratio depends in a complex way on the methanol content in methanol–apolar solvent mixtures; see ref 26b. (b). Clennan, E. L.; Yang, K. *Tetrahedron Lett.* **1993**, *34*, 1697.