The Photooxygenation of Benzyl, Heteroarylmethyl, and Allyl Sulfides

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Keywords: Oxygenations / Singlet Oxygen / Sulfides / Photochemistry

The photosensitised oxidation of benzyl ethyl sulfides in aprotic solvents (benzene or acetonitrile) gives the corresponding aldehydes under mild conditions. This is a general reaction which applies to benzyl derivatives containing either electron-donating or electron-withdrawing substituents and furthermore to hetero analogues such as 2-pyridinylmethyl sulfide (not to the 3-indolylmethyl sulfide, since reaction at the heterocycle moiety competes) as well as to allyl sulfides. In a protic solvent (methanol) these sulfides give the sulfoxides instead (except for the nitrobenzyl derivatives, where the aldehyde remains the major product). Among the α-substituted sulfides tested, the α-phenylbenzyl and the 3-cyclohexenyl sulfide give the corresponding ketone (the latter in a low yield), but the α-methylbenzyl sulfide gives the sulfoxide as the main product. The rate for singlet oxygen quenching and for chemical reaction have been measured for representative benzyl sulfides. The reaction is discussed in the frame of the currently accepted mechanism for sulfide photooxygenation. The key step for oxidative C–S bond cleavage appears to be hydrogen transfer from the activated α position in the first formed intermediate, the persulfoxide. This reaction is inhibited in methanol where the persulfoxide is hydrogen-bonded.

Introduction

Sulfides are well known to undergo smooth dye-photosensitised oxidation to give sulfoxides (the major products) and sulfones.[1] This reaction has been the subject of detailed mechanistic investigations. However, C−S bond cleavage occurs in some cases, as first shown by Corey and Ouannès in the case of benzyl sulfides.[2] These authors found that dibenzyl sulfide and some alkyl benzyl sulfides give benzaldehyde (45−75%) when reacting with singlet oxygen, produced both by radiofrequency electrodeless discharge or by dye-sensitised irradiation, along with sulfoxides and sulfones (25−55% overall). This reaction was confirmed and extended to 9-fluorenyl sulfide by Ando and coworkers,[3][4] who, also on the basis of the results they had obtained with some thiazolidines,[5] suggested that persulfoxides and *S*-hydroperoxysulfonium ylides are the key intermediates. However, the scope of this oxidative cleavage of sulfides has not been explored. Extension of this reaction is of interest in view of the mild condition typical of photosensitised oxygenation as a method for the preparation of aldehydes or at any rate as a synthetic path via sulfides. Thus, we carried out an explorative study on the photooxygenation of various substituted benzyl sulfides and extended it to heteroarylmethyl and allyl sulfides. The medium dependence of this reaction was also studied. It turned out that photooxidation in aprotic media is a reasonably general method for the preparation of aldehydes from sulfides (and, with some limitations, also of ketones from the corresponding α-substituted derivatives), whereas sulfoxides are generally the main products in protic solvents.

Results

Explorative Studies

A series of alkyl ethyl sulfides (**1**) with various alkyl groups was considered. This included benzyl (**1a−f**), allyl (**1g**, **h**) (in both cases α-unsubstituted as well as α-substituted derivatives were considered), as well as heteroarylmethyl sulfides (**1i**, **j**). In explorative studies, 0.01 M oxygen-equilibrated solutions of the sulfides in benzene, acetonitrile or methanol containing triphenylporphine (for the first solvent) or Rose Bengal as the sensitizer were irradiated in the visible (under this condition, light was absorbed only by the sensitiser).

From all of the benzyl sulfides (**1a−d**, **1f**) the main products from the oxygenation both in benzene and in acetonitrile were the corresponding aryl aldehydes (**2a−d**) and ketones (**2f**) resulting from oxidative C−S bond cleavage, with a minor amount of the sulfoxides **3** and sulfones **4** arising from sulfur atom oxygenation (Scheme 1). In the case of **1a** the time evolution of the photooxygenation was followed, and it was noticed that sulfoxide **3a** was negligible at low conversion, and its amount increased during the conversion, though it always remained a minor product. A trace (≤ 0.5%) of the corresponding bibenzyl was formed from most sulfides. An exception to the general behaviour was the α-methylbenzyl sulfide **1e**, from which only a small amount of acetophenone (**2e**) was formed in benzene, while the main product was sulfoxide **3e**.

With **1a** and **1b** the product distribution changed in methanol and the corresponding sulfoxides **3a**, **b** became the main products. The change in product distribution occurred in neat methanol or with a large amount (e.g. 30%) of MeOH as co-solvent with benzene, while when only a small (e.g. 0.5%) amount was added the products were the same as in neat benzene. Furthermore, this change did not occur with all of the benzyl sulfides: With the two nitrated

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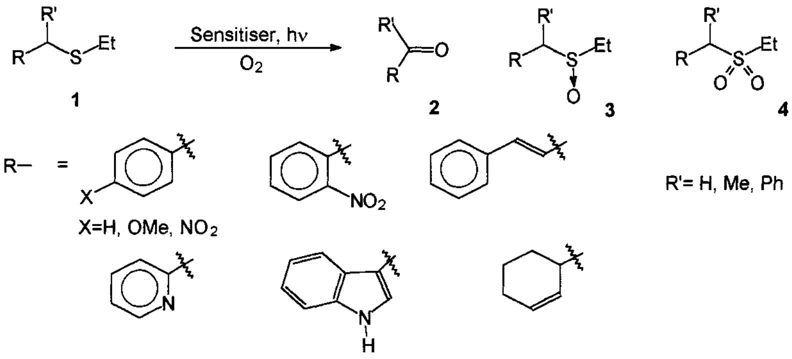


Scheme 1. Products obtained by the dye-sensitised oxidation of ethyl sulfides **1**

Table 1. Products obtained by the dye-sensitized oxidation of ethyl sulfides **1**[a]

Substrate	R	R′	Solvent	% Sulfide converted	Products (% yield) **2**	**3**	**4**
a. Benzyl sulfides							
1a	Ph	H	Benzene	24	80	3	8
			MeCN	35	76	8	5
			MeOH	87	18	65	10
1b	4-MeOC$_6$H$_4$	H	Benzene	36	85	2	8
			MeCN	40	78	4	5
			MeOH	83	10	55	7
1c	4-NO$_2$C$_6$H$_4$	H	Benzene	15	83	7	–
			MeCN	22	75	4	–
			MeOH	20	44	3	–
1d	2- NO$_2$C$_6$H$_4$	H	Benzene	31	70	7	7
			MeOH	34	30	–	–
1e	Ph	Me	Benzene	14	10	70	5
			MeOH	55	2	65	–
1f	Ph	Ph	Benzene	20	60	9	22
			MeOH	75	40	3	–
b. Allyl sulfides							
1g	PhCH=CH	H	Benzene	60	45	7	4
			MeOH	78	5	70	15
1h	−CH=CH−[CH$_2$]$_3$−		Benzene	25	20	6	–
			MeOH	87	7	20	
c. Heteroarylmethyl sulfides							
1i	2-Pyridyl	H	Benzene	45	70	25	–
			MeOH	55	3	74	–
1j	3-Indolyl	H	Benzene	27	10	–	–
			MeOH	55	3	–	–

[a] As obtained by 10 min of irradiation of a 0.01 M solution.

derivatives **1c** and **1d** and with the benzhydryl sulfide **1f** the sulfoxide was not formed and the aldehydes or ketones **2** were the main products also in methanol. In this solvent the yield of **2** was lower, probably because secondary photodecoposition of the primarily formed carbonyl derivatives was significant in this case.

The same medium-dependent reaction course as with benzyl sulfides **1a**, **b** was observed also with the cinnamyl sulfide **1g**, with the 2-pyridylmethyl sulfide **1i** and, though with low overall yield, with the aliphatic allyl sulfide **1h**. The 3-indolyl sulfide **1j** gave only 10% of the aldehyde **2j**. In order to compare the reactivity of the substrates, the results obtained by 10 min irradiation − which involved a conversion ranging from 14 to 87% − are gathered in Table 1.

Preparative Experiments

Since, as mentioned above, aldehydes were in several cases obtained in a fair yield in benzene or MeCN, it was tested whether this could lead to a preparatively useful procedure for aldehydes. Thus, the irradiation was carried out on 100 mL of a 0.1 M solution of sulfides **1a**, **b**, **c**, **i** in an immersion-well apparatus by means of a mercury arc. The oxygenation was carried out up to almost complete conversion, the solvent was evaporated and the residue was bulb-to-bulb distilled under reduced pressure. In this way benzaldehyde (**2a**) and its *p*-methoxy (**2b**) and *p*-nitro (**2c**) derivatives as well as 2-pyridinecarbaldehyde (**2i**) were obtained from the corresponding sulfides in a 0.5- to 1-g amount and

Table 2. Rate constants for the reaction of singlet oxygen with the sulfides **1a−c**

Substrate	Solvent	k_T [$M^{-1}s^{-1}$][a]	k_r [$M^{-1}s^{-1}$][b]
1a	Benzene	1.14×10^7	0.55×10^7
	MeCN	1.22	0.61
	MeOH	0.94	1.2
1b	Benzene	1.66	0.52
	MeCN	1.37	0.34
	MeOH	1.40	1.65
1c	Benzene	0.17	0.10
	MeCN	0.28	0.23
	MeOH	0.13	0.14

[a] Total quenching rate constant, as determined by measuring of the singlet oxygen lifetime through the emission at 1270 nm. − [b] Chemical reaction rate constant, as measured in competition experiments in the presence of octaline, $k_r = 1.84{\cdot}10^6\ M^{-1}s^{-1}$, ref.[6] Average of at least 3 experiments within 5%.

with a yield of 52, 60, 62, and 55%, respectively, through a simple procedure that may be easily scaled up (see Experimental Section).

Kinetic Data

In order to obtain mechanistic information the two key kinetic parameters, viz the total (physical + chemical, Equations 1, 2) quenching rate of singlet oxygen by the sulfides ($k_T = k_q + k_r$) and the rate of chemical reaction (k_r) were measured in representative cases, viz for the three benzyl sulfides **1a−c**.

$${}^1O_2 + R_2S \rightarrow {}^3O_2 + R_2S \qquad (1, \text{rate constant } k_q)$$

$${}^1O_2 + R_2S \rightarrow \text{Products} \qquad (2, \text{rate constant } k_r)$$

The value of k_T was directly determined by laser flash photolysis through the quenching of the singlet oxygen produced by phenalenone sensitisation and that of k_r by determining the competitive reaction of the same sulfides and octaline (assumed to add singlet oxygen at a solvent-independent rate) in low-conversion experiments according to the method introduced by Foote.[6] The data in three solvents, benzene, acetonitrile and methanol, are reported in Table 2.

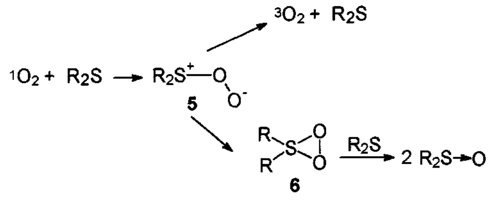
Discussion

Inspection of Table 1 shows that the oxidative cleavage first reported by Corey[2] is in fact a general reaction of benzyl sulfides, tolerant of ring substitution. All of the α-unsubstituted derivatives give moderate to good yields of the aldehydes when the irradiation is carried out in aprotic (both polar and apolar) solvents such as benzene or acetonitrile. This may be a convenient way to prepare aldehydes, since visible light absorbed only by the sensitizer is used − so that no direct photochemical reaction of the substrate takes place − and the reaction occurs under the peculiarly mild condition of photochemical reactions. As shown in a number of representative cases, this preparation of aldehydes can be conveniently carried out on a gram scale.

With some of these sulfides, the course of the reaction changes in protic solvents, where the sulfoxides − i.e. the same products which are obtained from dialkyl sulfides − are the main products. With the nitro derivatives **1c** and **1d**, however, the aldehydes remain the main products also in methanol, though with a lower yield probably due to secondary photodecomposition.

This oxidative cleavage and the characteristic solvent dependence are not limited to benzyl sulfides. Thus, aldehydes or sulfoxides depending on the solvent are obtained also from a hetero analogue such as the 2-pyridylmethyl sulfide **1i** (from the 3-indolylmethyl derivative **1j** the yield of aldehyde is poor; however, see below) and from allyl derivatives, with a satisfactorily yield from cinnamyl sulfide **1g** and a poor yield from the 3-cyclohexenyl sulfide **1h**. As for the two α-substituted benzyl sulfides, the benzhydryl sulfide **1f** gives ketone **2f**, while with the α-methylbenzyl sulfide **1e** sulfoxide **3e** is the main product with only 10% of **2e**. In some cases the sulfone is also a significant product (noteworthy, 22% of **4e** from **1e).**

The present results with benzyl sulfides and related derivatives can be discussed with reference to the generally accepted mechanism for the photosensitised oxidation of dialkyl sulfides.[1] These give the sulfoxides under all conditions, but the efficiency of the reaction is known to be medium-dependent. More precisely, the total rate of singlet oxygen quenching ($k_T = k_q + k_r$, see Equations 1, 2) does not change, while the rate of the chemical reaction (k_r) is much higher in protic than in aprotic solvents.[1a,7,8] This is currently explained by admitting the intermediacy of persulfoxide **5** (see Scheme 2), although such a species has never been directly detected. In aprotic media this mainly collapses to unchanged sulfide and triplet oxygen, and in part ($k_r \leq 5\%\ k_d$, see Scheme 2) rearranges to a further intermediate, usually assumed to be the thiadioxirane **6** (see below, however). This in turn transfers an oxygen atom to a sulfide giving two sulfoxide molecules. Protic solvents, on the other hand, preclude unproductive decay and make formation of the sulfoxide much more effective.[1a,7,8]

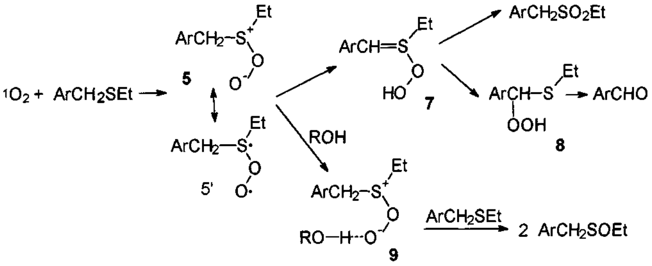


Scheme 2. Mechanism for the photooxidation of alkyl sulfides

Table 2 shows that quenching of singlet oxygen by benzyl ethyl sulfide **1a** occurs at a rate ($k_T = 1.14{\cdot}10^7\ M^{-1}s^{-1}$ in benzene, see Table 2) in the same order as that of simple alkyl sulfides (e.g., for Et_2S: $k_T = 1.7$, 2.0, or $3.04{\cdot}10^7\ M^{-1}s^{-1}$ has been reported).[8−11] Singlet oxygen is an electrophile and reacts faster with electron-rich substrates. Accordingly, ring substitution affects the k_T rate in the expected way with these benzyl sulfides, 4-MeO > H > 4-O_2N, see Table 2. The methylene group interposed between the ring and the sulfur atom reduces the effect relative to that observed for phenyl sulfides (a methoxy group in **4** increases k_T by a factor of 3.5 in thioanisole,[12] by a factor of 1.45 in benzyl sulfide **1**). Table 2 shows that quenching is little solvent-dependent, as is generally assumed[8] to be the case for alkyl sulfides.

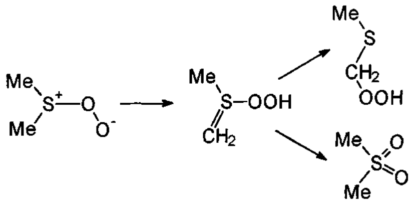
The chemical reaction of benzyl sulfides differs from that of dialkyl sulfides both quantitatively and qualitatively. With Et_2S, as an example, the product of sensitised oxygenation remains the sulfoxide under all conditions, but its rate of formation (k_r) strongly increases (by a factor of ca. 15, from $3.8 \cdot 10^6$ to $\geq 5.6 \cdot 10^7$ $\mathrm{M}^{-1}\mathrm{s}^{-1}$) in going from benzene to methanol.[8] With the benzyl sulfides in Table 2 the rate of reaction k_r accounts for a large fraction of the total quenching (k_T) in benzene (32% with **1b**, 70% with **1c**, see Table 2, instead of $\leq$ 5% of Et_2S). Furthermore, the k_r increase in MeOH is moderate (by a factor of 2 with **1a**, 3 with **1b**, 1.4 with **1c**) but involves a change in the product distribution (except for **1c**).

As for the mechanism of C−S cleavage, Ando showed that the sensitised oxidation of a series of thiazolidines leads to α-hydroperoxysulfides via a strongly oxidising intermediate, suggested to be an *S*-hydroperoxysulfonium ylide.[4] He found that the oxidation of benzyl sulfide also produces an oxidising intermediate (it reacts with Me_2S) and therefore suggested that benzaldehyde is formed from the persulfoxide via ylide **7** and hydroperoxide **8** as shown in Scheme 3.[4] This is reasonable; in accord with the intermediacy of the ylide, we observe that the proportion of sulfoxide **3a** from **1a** in apolar solvents grows somewhat with increasing conversion, probably by secondary oxidation of **1a** by **7**.



Scheme 3. Mechanism for the photooxidation of benzyl alkyl sulfides

Recent computations[13] generalized the argument, suggesting that the persulfoxide from dimethyl sulfide may also rearrange to the corresponding ylide, not to the thiadioxirane as previously assumed, and that this may be the path leading to the sulfone (for this point there is also some experimental evidence)[14] as well as to the α-hydroperoxide (Scheme 4). It remained unclear whether the ylide may also be involved in the formation of the sulfoxide. As mentioned above, with dialkyl sulfides all of these paths are unimportant, however. It appears that with the present substrates the weak (benzylic or allylic) α-C−H bond makes rearrangement to ylide **7** faster and thus a better competitor for decay of the persulfoxide to the components. This can be understood with reference to the mixed zwitterion − diradical nature (see Scheme 3, mesomeric formulae **5** ↔ **5′**) of the persulfoxide, as in general of 1,3-dipoles.[15a] Noteworthy, the ratio k_r/k_T, which may be taken as a rough estimate of the propensity of the persulfoxide to react chemically rather than decay to the components, only marginally increases both in the series **1b** < **1a** < **1c** and in polar MeCN relative to benzene. Thus, polar factors have a slight effect on the rearrangement efficiency, and it is the homolytic strength of the C−H bond that matters (only in the case of the less activated **1c** polar acetonitrile does double the rate of reaction with respect to benzene, which provides evidence for some polar effect). A different homolytic fragmentation of the ylide reasonably originates the observed trace of bibenzyl.



Scheme 4. Alternative paths from the persulfoxide

The easy formation of the ylide explains most of the results, but two points need further consideration. First, the α-methyl sulfide **1e** gives the sulfoxide as the main product, not the ketone (while the α-phenyl sulfide **1f** behaves as the α-unsubstituted derivatives). It may be that the methyl group disfavours the conformation suitable for hydrogen transfer in the persulfoxide and makes this process too slow to compete with some other path leading to the sulfoxide. We are currently carrying out a computational analysis of the persulfoxide conformation in order to support this hypothesis.[15b]

Alternatively, it may be that the ylide is formed but does not rearrange to the hydroperoxide. As mentioned above, calculations suggest that a viable path for the ylide is rearrangement to the sulfone.[13] With the present benzyl derivatives sulfones are often significant products (5−10%) and this is the second noteworthy point. The fact that the sulfide for which the maximum yield of sulfone obtained is **1f** (22% **4f** in benzene), for which a decrease of the cleavage to the ketone to 60% (from 80% with **1a**) is observed, suggests that this is indeed an alternative path from the ylide.

In protic (not in polar) solvents the efficiency of the reaction increases and *S*-oxygenation becomes the main process with most of the above sulfides. Mechanistic studies on the oxygenation of Et_2S in methanol by Foote[7] and Clennan[8][16] suggested that under these conditions the solvent forms a hydrogen bond with the persulfoxide (formula **9** in Scheme 3) or adds to it (to give a hydroperoxy alkoxy sulfide. The former hypothesis is simpler and explains the present results. Indeed, it is reasonable that when the outer oxygen atom of the persulfoxide is involved in a hydrogen bond, intramolecular hydrogen-transfer to give **7** does not occur, and the reaction rather is electrophilic oxygen transfer to a second molecule of sulfide (to give ultimately two molecules of sulfoxide, see Scheme 3).

Some points are worth noticing with respect to the protonation of the persulfoxide. This is a weak base, as indicated by the fact that the change in the product distribution (from aldehydes to sulfoxides) requires a large amount of MeOH as co-solvent, while 0.5% has no effect. This indicates that the intermediate is quite short-lived or it is protonated at a rate below diffusion control. For the case of **1a**, the latter hypothesis has been supported through a more detailed examination of this point.[17] With the nitro-substituted derivatives **1c** and **1d**, the electron-withdrawing substituent is expected to limit charge localisation of the negative charge on the outer oxygen atom and thus to make the persulfoxide still less basic. In fact, with these derivatives the rate of photooxygenation in MeOH increases less than with **1a** and the benzaldehyde remains an important product.

Finally, two of the sulfides we considered, **1h** and **1j**, did not undergo any of the above reactions in a satisfactorily yield. This is due the occurrence of alternative processes. These were not investigated, but may have been expected in these cases. As for **1h**, Clennan demonstrated that in aliphatic allyl sulfides the C=C bond participates in the reaction[16b,c] and different products are formed. Remarkably, with a cinnamyl rather than an aliphatic allyl group both of the general reactions, oxidative cleavage in aprotic and *S*-oxidation in protic media, occur unperturbed (see **1g** in Table 1). In the case of **1g** again a different process is expected to intervene because of the known sensitivity of the indole ring to singlet oxygen.[18]

Conclusion

The photooxidative cleavage of benzyl sulfides first reported by Corey is in fact a general reaction for all substrates containing an activated α-hydrogen atom. Benzyl (independently from ring substitution), heteroarylmethyl (provided that the heterocycle is not itself reactive with $^1O_2$) and phenylallyl sulfides all give the corresponding aldehydes in a fair yield by reaction with singlet oxygen in aprotic solvents. The production of ketones from α-substituted sulfides appears to be subjected to some limitations. At least for aldehydes, the generality and simplicity of the reaction, the mild conditions involved and the wide applicability due to the resistance of most organic functions to $^1O_2$ and the lack of influence of ring-substitution suggest that the above procedure may be proposed as a method for their preparation from sulfides. This may be a mild alternative to other known methods for the overall conversion of a halide to an aldehyde.

In methanol, reaction with singlet oxygen in most cases leads to sulfoxides. This reaction may also be of some interest, for example in view of the fact that *S*-oxidation occurs under mild conditions and, in the case of the pyridinemethyl sulfide **1i**, with no competition by *N*-oxidation.

The observed chemistry fits in the frame of the generally accepted mechanism for sulfide oxidation, with the difference that an activated α-C−H bond makes homolytic hydrogen transfer the predominant reaction from the persulfoxide. The highly effective oxygenation of benzyl sulfides and their heteroaryl analogues discussed here may be relevant for biological systems.

Experimental Section

General Remarks: Spectroscopic-grade solvents were used. Benzene and acetonitrile were distilled from calcium hydride before use. The sulfides **1a**,[19] **1b**,[20] **1c**,[21] **1d**, **e**,[22] **1f**,[23] **1g**,[24] **1h**,[25] and **1i**[26] were prepared from the condensation of the appropriate chlorides or bromides and sulfides according to published procedures. The heterocyclic derivative **1j**[27] was prepared from indole as reported. Samples of the sulfoxides **3a−i**[28−30] and sulfones **4a−i**[20,22,24,30−34] for the comparison with the photoproducts were prepared by 3-chloroperbenzoic acid or acetic acid/hydrogen peroxide oxidation according to the general procedure.[35] Rose Bengal, tetraphenylporphine and 1,2,3,4,5,6,7,8-octahydronaphthalene were commercial products (Aldrich).

Photochemical Reactions: Explorative irradiations (see Table 1) in the presence of the appropriate sensitiser were carried out in rubber-stoppered Pyrex tubes for 10 min while passing a stream of oxygen saturated with the solvent through the solutions. 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. − Kinetic measurements were carried out in the same way in the presence of octaline and the reactions were discontinued at ≤ 20% conversion. The solution was treated with triphenylphosphane before analysis in order to reduce the hydroperoxide to the allylic alcohol and then analysed as above. The data reported in Table 2 are the average of at least three measurements within 5%.

Benzaldehyde: A solution of 1.52 g of benzyl ethyl sulfide (**1a**, 0.1 M) and 50 mg of TPP in 100 mL of benzene was irradiated for 5 h in a water-cooled immersion-well apparatus fitted with a high-pressure mercury arc (Helios Italquartz, 150 W) through an uranyl filter ($\lambda_{tr} > 400$ nm) while passing a slow stream of oxygen through the solution. The solvent was removed by rotary evaporation and the residue distilled to give 0.55 g (52% yield) benzaldehyde. The reaction was carried out analogously with sulfides **1b**, **c**, and **i** to give the corresponding aldehydes in the 60, 62, and 55% yield, respectively.

Analytical Methods: Gas-chromatographic determinations were carried out by means of a Hewlett Packard Mod. 5890 with an Innowax column (30 m × 0.25 mm, 0.5 μm film thickness) and He as the carrier gas. The injector pressure was constant (12 ψ). The temperature program was 50−140 °C (5 °C/min), 140−250°C (25 °C/min, 7 min final time). For mass determinations this was equipped with a Mod. 5971 mass detector.

Photophysical Measurements: Rate constants for the quenching of singlet oxygen were measured by Prof. G. Aloisi and F. Elisei at the Dept. of Chemistry, University of Perugia. This was done by laser pulse spectroscopy (Spectra Physics Nd:YAG laser), by measuring the emission lifetime at 1270 nm after sensitization by phenalenone.[36]

Acknowledgments

S. M. B. (permanent address: Department of Organic Chemistry, University of Buenos Aires, Ciudad Universitaria, CP1428 Buenos

Aires, Argentina) thanks FOMEC for a fellowship. R. T. thanks Prochimica for a fellowship. Dr. P. P. Rossi (Prochimica) is thanked for discussing this project. Financial support by Consiglio Nazionale delle Ricerche, Rome, is gratefully acknowledged.

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Received November 30, 1998
[O98541]