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Photochemistry and Photophysics of Aromatic Sulfoxides. 3. α-Cleavage and the Role of the Sulfenic Ester†

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The photochemistry of aryl benzyl sulfoxides is described. The initial event is homolytic cleavage to form a singlet sulfinyl/benzyl radical pair. This radical pair partitions between reversion to starting material with at least partial racemization and closure to form a sulfenic ester. With acetone sensitization, the primary radical pair also undergoes quite significant escape, leading to formation of diphenylethane and aryl arenethiosulfonates. Secondary photolysis of the sulfenic ester leads exclusively to S−O homolysis, yielding the radical pair from which isolated products are derived. Quantum yields and other mechanistic observations are discussed.

Introduction

A common mechanistic assumption for many photochemical reactions of sulfoxides is that the first step is homolytic cleavage of a C−S bond, or α-cleavage.[1] A significant subset of this chemistry, in which the S−O bond has been broken but both atoms remain in the isolated structures, has been proposed to go through a sulfenic ester (RSOR'), whose secondary chemistry leads to the observed products.[2−7] Quite recently, sulfenic esters themselves were isolated in 45−67% yield after photolysis of a carbonyl containing cyclic sulfoxide,[8] and very modest yields in other cyclic cases have been isolated previously.[6,9,10] Examples of transformations in which the sulfoxide → sulfenate → products pathway has been proposed are shown in Figure 1.

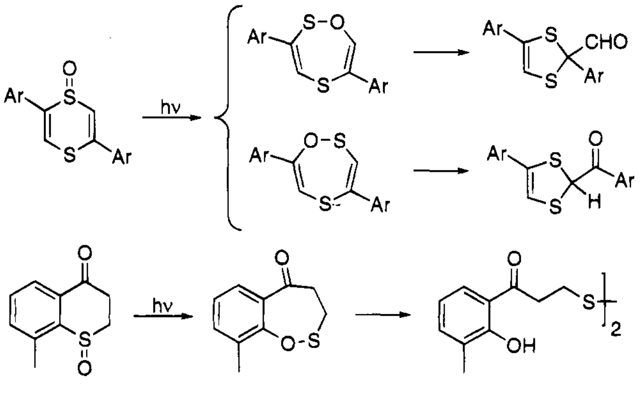
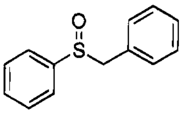
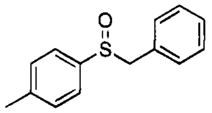


Figure 1. Examples of transformations which have been proposed to go through α-cleavage and sulfenic esters.[3,5]

Many substantive questions remain about this pathway, even if taken at face value. For example: (1) What, if any, is the role of the sulfenic ester in sulfoxide photoracemization? (2) Does the formation of the sulfenic ester really involve a radical pair? (3) Is the formation of the sulfenic ester photochemically reversible? (4) Does efficient formation of the sulfenic ester depend on the sulfoxide being cyclic? (5) Are the factors which affect sulfoxide cleavage selectivity the same as those for ketone photochemistry? As part of an attempt to clarify the photochemistry of aromatic sulfoxides in general, we report the photochemistry of benzyl phenyl sulfoxide (**1a**) and benzyl *p*-tolyl sulfoxide (**1b**). These molecules serve as archetypes of acyclic sulfoxide structures strongly biased toward α-cleavage. We confirm the intermediacy of the sulfenic ester in this chemistry and give clear answers to several of these questions.


1a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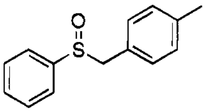
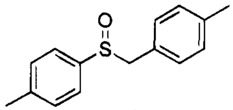
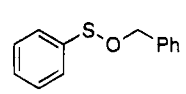
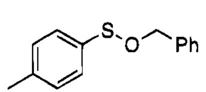

1c


1d



2a



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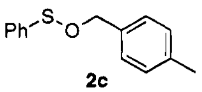

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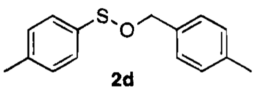

2d

Results

Photolysis of **1** until all of the starting material is consumed generates a complex reaction mixture whose composition depends on several parameters, including the reactivity and viscosity of the solvent and the wavelength of excitation. The complex reaction mixture is largely a result of secondary and tertiary photolysis. Also, some of the sulfur-containing products appear to undergo complex redox equilibria and/or to scavenge O_2

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† Dedicated to Professor Glen A. Russell on the occasion of his 70th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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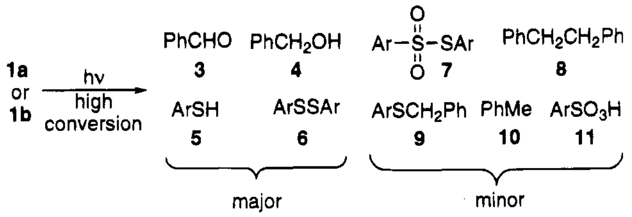

Figure 2. Products observed on extended photolysis of **1a** (Ar = Ph) and **1b** (Ar = *p*-tolyl).

which remains in trace quantity after Ar flushing or is introduced on workup and analysis. Typical components of the mixture obtained in inert solvent are illustrated in Figure 2. To avoid the secondary photolysis problem, the reactions reported here were carried out to modest conversions, generally ≤20%. Starting concentrations for solution work were all 3–6 mM.

Compounds **1** are particularly susceptible to secondary photolysis at lower energy wavelengths, as several of the photoproducts have larger absorption extinction coefficients at wavelengths above approximately 290 nm. In fact, early experiments, carried out with excitation provided by the very broad output of the "300 nm" bulbs of a Rayonet photoreactor, led to reaction mixtures which contained very little or no **2**, even at low conversion. Independent synthesis of compounds **2** showed them to be stable to the analysis conditions and revealed the large difference in absorption coefficient for **1** and **2**. It became clear that compounds **2** were probably being formed, but were being selectively photolyzed because of the wavelengths of excitation. The problem was alleviated by tuning the excitation wavelength to a more appropriate value. Photolyses in which the data of interest concerned the transformation of **1** to **2** were carried out using the output of a 150 W Xe lamp filtered through a monochromator which could be set to more convenient wavelengths, generally 267 nm. Experiments concerned with the ultimate photoproducts were carried out using either the Xe lamp setup or the Rayonet as indicated. The UV spectra of **1a**, **2a**, and benzaldehyde are shown in Figure 3 for comparison.

Exploratory photolysis of **1** was carried out in several solvents using both the Rayonet 300 nm excitation and the Xe lamp/monochromator setup. Two effects of solvent were observed. The first is the trivial reaction of several products or intermediates with solvents. For example, rather than benzaldehyde, its methyl acetal was detected when the reaction was carried out in methanol. Secondly, there was correlation between "clean" reactions and relatively high solvent viscosity. It was observed, for instance, that the quantity of benzyl alcohol increased at the expense of benzaldehyde when viscosity is lowered. Disulfides **6** increased at the expense of arenethiols **5**; the amount of minor products **7** and **8** and the number and amount of unidentified trace compounds also correlated inversely with viscosity. Taking the viscosity argument to the extreme, photolyses of solid **1b** were also carried out, both as a KBr pellet at room temperature and as the neat solid at 77 K, using Rayonet 300 nm excitation. Only **3**, **5b**, and **6b** were observed as products. This phenomenon is illustrated by the product distributions given in Table 1, which are for reactions of **1b** in "inert" solvents. The trends in these data are much more important than the precise numbers, since the latter are so dependent on excitation conditions and conversion. It should also be pointed out that we view the relative quantities of **5** and **6** given in Table 1 and elsewhere in this paper with extreme caution. We did not take extreme measures to exclude O_2 from our reactions and analysis solvents and view it as quite likely that the amounts of **5** reported are underestimates of the "true" values, while those of **6** are overestimates. Indeed, control experiments subjecting dilute solutions of **5** to our standard handling and analysis conditions showed some conversion to **6**.

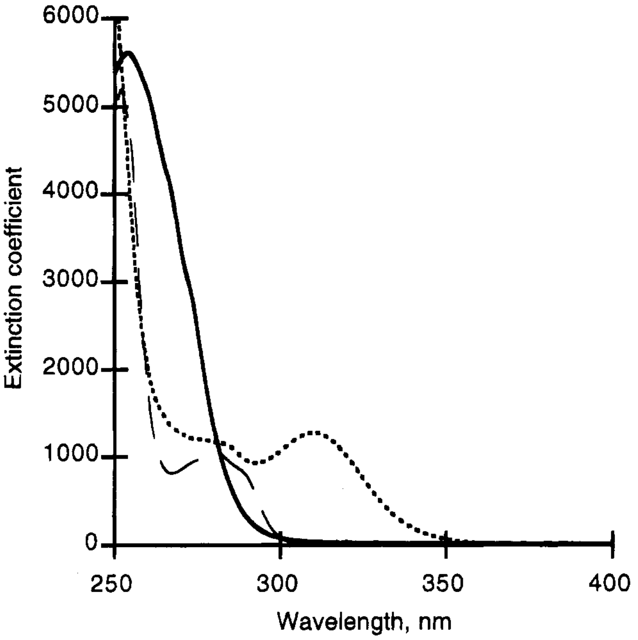

Figure 3. UV spectra of phenyl benzyl sulfoxide (**1a**, solid line), benzyl benzenesulfenate (**2a**, dotted line), and benzaldehyde (**3**, dashed line) in acetonitrile. A *ca.* 5 nm red shift is observed in the sulfoxide spectrum in nonpolar solvents. The sulfenic ester used here was approximately 90% pure, but the spectrum is nearly identical to those collected on HPLC runs with diode aray detection of the pure sulfenic ester peak.

Table 1. Product Distributions from Photolysis of 1b to Modest Conversions in Several Solvents

solvent	conversion[a] (%)	rel product yields[b] (%)						
		2b	**3**	**4**	**5b**[c]	**6b**[c]	**7b**	**8**
2-methyl-2-propanol[d]	5	100						
2-methyl-2-propanol[d]	15	74	11	6		5	4	
acetonitrile	7	72					19	9
acetonitrile	24	73	6			2	12	7
acetone	5		33	9		3	23	32
acetone	20		32	17		4	17	30
neat (KBr)[e]	5		50		45	5		
neat (77 K)[e]	10		51		44	5		

[a] Determined by comparison to inert internal standard unless otherwise noted. [b] The sum of these product mole fractions is set to 100%. Mass balances for the "benzyl half" of the molecule are over 90%; those for the arylsulfinyl portion of the molecule are generally lower, as can be seen from the data. Trace products are not included in the table. Excitation from Xe lamp with monochromator set to 267 nm unless otherwise noted. [c] These values almost certainly underestimate the quantity of **5b** and overestimate **6b** formed as a result of the chemistry of interest. See text. [d] 1% water added. [e] No internal standard used. Conversion estimated by comparison of product integrations to total. Excitation provided by Rayonet 300 nm bulbs.

Given the solvent reactivity and viscosity effects, 2-methyl-2-propanol, spiked with 1% H_2O, was chosen as the solvent for the majority of our solution studies. It is relatively viscous and did not introduce any new products into the mixture. Even extended photolyses resulted in fairly clean product mixtures. The progress

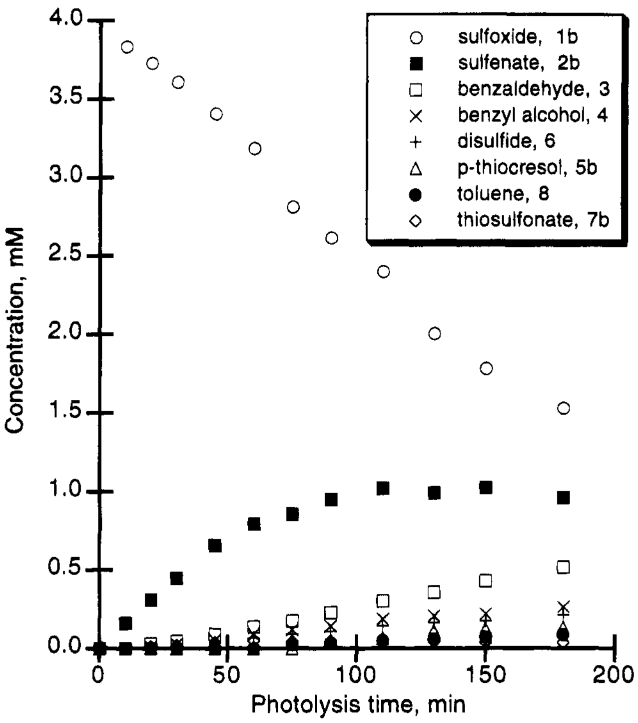

Figure 4. Reaction mixture as a function of photolysis time for a solution of **1b** in 2-methyl-2-propanol, using light centered at 267 nm. Note that for photolysis times up to *ca.* 30 min, sulfenate **2b** is virtually the sole product. Points are averages of at least two HPLC determinations.

of the photolysis of **1b** in 2-methyl-2-propanol as a function of time is shown in Figure 4, which also illustrates the meaninglessness of a single quantitative description of the product mixture. Perhaps the most valuable information from Figure 4 is that the initial product from photolysis of **1b** in 2-methyl-2-propanol is exclusively the sulfenic ester **2b**. Products such as benzaldehyde and disulfide **6b** are clearly a result of a *second* photochemical event.

Since the appearance of easily isolable products such as benzaldehyde and thiophenol was determined to be a multiphoton event, the meaningful quantum yields are those for the loss of starting materials **1** and the formation of the sulfenic esters **2**. Though compounds **2** were amenable to analysis, particularly by reversed phase HPLC, we were unable to obtain macroscopic samples of these materials in purities higher than about 90%. The difficulty in handling benzenesulfenic esters has been noted by other authors.[11] Various methods for purification always led to decomposition such that the total purity was never improved beyond that which was obtained from the crude synthetic reaction mixture. Though we felt comfortable using calibration curves from this material for Figure 4, it was decided to measure the quantum yield of decomposition of **1**, Φ_{loss}, rather than the appearance of **2**. Nonetheless, it should be noted that only in low viscosity solvents, such as acetonitrile, did any other one-photon product contribute to the product mixture in any but trace amounts. The observed quantum yields, measured against azoxybenzene as an actinometer, are shown in Table 2.

Double label experiments were carried out in order to gain further evidence for radical pairs as intermediates.

Table 2. Quantum Yields for Disappearance of Starting Materials[a]

compd	solvent	wavelength[b] (nm)	Φ_{loss}[c]	$\Phi_{\mathrm{rot.}}$[d]
1a	acetonitrile	267	0.28	
1b	acetonitrile	267	0.29	0.53
1b	2-propanol	267	0.30	0.44
1a	2-methyl-2-propanol	267	0.20	
1b	2-methyl-2-propanol	267	0.21	0.42
1b	acetone	267	0.33	0.41
2a	2-methyl-2-propanol	313	0.69	

[a] All solutions were originally 4–6 mM in starting material and were flushed with Ar to remove oxygen. Under these conditions, all of the light is absorbed. [b] Light was provided by a 150 W Xe lamp filtered through a monochromator set at this wavelength with 24 nm total linear dispersion. [c] Azoxybenzene was the actinometer. Estimated error: ±20%. [d] Measured relative to Φ_{loss}.

Solutions containing 2 mM each of **1b** and **1c** were photolyzed to low conversion in three solvents: acetonitrile, 2-methyl-2-propanol, and acetone. In each case, the resulting solutions were analyzed for all four sulfoxides **1a**–**d**, the corresponding sulfenic esters, and bibenzyls. In 2-methyl-2-propanol, no "cross-products" were observed. In acetonitrile, "cross" sulfoxides **1a** and **1d** were formed in equal quantities, each accounting for 7% of the loss of starting materials. Cross sulfenic esters **2a** and **2d** were also observed, each accounting for 6% each of the loss of starting materials. In acetone, no sulfenic esters were observed (*vide infra*), but sulfoxides **1a** and **1d** accounted for 24% of lost starting material. Additionally, bibenzyl (**8**), *p*-methylbibenzyl, and *p,p'*-dimethylbibenzyl were found in a 1:2:1 ratio and accounted for 20% of lost starting materials.

The optical activity of sulfoxides **1** gives the researcher a tool to determine if there are any racemic intermediates which may partition between product formation and returning to starting material. Thus, in addition to the quantum yield for chemical loss of **1** (Φ_{loss}), the quantum yield for loss of optical activity of **1b** was measured by following the optical rotation of the sample as a function of photolysis time while simultaneously monitoring the chemical composition by HPLC. Optically pure (>98% as judged by rotation) (*S*)-**1b** was prepared by standard literature methodology.[12] In order to increase the signal to noise ratio of the rotation data while still doing the experiments at low concentration, the measurements were taken at the highest energy wavelength available on the polarimeter, which was 405 nm. Since none of the observed products are chiral, it was assumed that loss of starting material would present a proportional loss in rotation. Rotation losses *in excess of that which could be accommodated by chemical conversion* were attributed to partial racemization of **1b**, as is discussed below. The quantum yield for total loss of rotation, Φ_{rot}, is given in Table 1.

The triplet energies of alkyl phenyl sulfoxides are rather high, of the order of 80 kcal/mol. Very similar phosphorescence spectra were obtained for **1** as for phenyl methyl sulfoxide.[13] This severely limits the choice of triplet sensitizers. This is an important consideration, since a number of reports in the literature show sulfoxide chemistry in cases where triplet sensitization is unlikely

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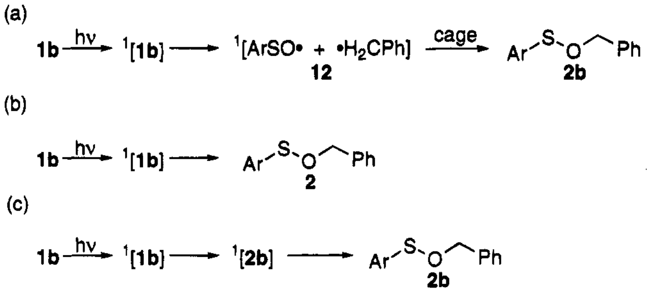

Figure 5. Possible mechanisms for the transformation of sulfoxides to sulfenic esters, using **2b** as the example.

to be the mechanism for energetic reasons.[2,14-18] While the actual mechanism of such chemistry is not clear at this time, we wished to avoid such alternate pathways. In order to carry out triplet-sensitized reactions, we used acetone, with a triplet energy of about 79 kcal/mol, as both solvent and sensitizer. The initial product distribution on photolysis in acetone is significantly different from that of any other solvent, with substantially more **7** and **8**, as seen in Table 1. The apparent quantum yields Φ_{loss} and $\Phi_{\text{rot.}}$ in acetone are shown in Table 2.

Direct photolysis of compounds **2** yields product mixtures very similar to those found on extended photolyses of **1**. By purposefully carrying out photolyses of **2** at wavelengths where the extinction coefficients of **1** are very low, it is straightforward to photolyze the sulfenic esters without affecting any sulfoxide which might be formed. Significantly, no sulfoxide was observed; only products deriving from S–O bond cleavage were found.

Discussion

Mechanism of Sulfenic Ester Formation. The nearly quantitative formation of sulfenic esters **2** on photolysis of **1** is documented in Figure 4. Because of the apparent generality in sulfoxide photochemistry, it is important to consider various mechanisms for the transformation of **1** to **2**. The answer will have implications for the development of a working paradigm for α-cleavage in sulfoxides and for sulfoxide racemization.

The thermal chemistry of **1b** has been well documented by Mislow and co-workers.[19,20] The racemization of **1b** was found to be due to homolytic cleavage of the S–CH$_2$ bond to form the same sulfinyl/benzyl radical pair **12** as is shown in Figure 5a. Random reclosure leads to loss of configuration at both the sulfur atom and the CH$_2$ at equal rates.[21] However, it was also concluded that the reversible thermal rearrangement of **1b** and **2b** does *not* pass through a radical pair intermediate, based largely on a small, negative activation entropy.[19] The existence of such a pathway on the ground state surface led us to consider whether there might be similar rearrangements, with lower activation energy, on excited state surfaces. In the event, adiabatic rearrangement shown in Figure 5c can be eliminated as a significant pathway. Formation of **2** in its excited state by photolysis of **1** would be expected to behave very much like direct photolysis of **2**, but this is not observed; *only* **2** is formed during the initial stage of photolysis in 2-methyl-2-propanol. Benzaldehyde and thiophenol are *two* photon products of **1a**.

The nonadiabatic rearrangement of **1** to **2**, shown as Figure 5b, is also unlikely to be significant. This conclusion is based on the observation of **7** and **8** when the photolysis is carried out in low viscosity solvents. These products are only consistent with S–C bond cleavage, followed by escape to form freely diffusing radical pairs. (Thiosulfonates are known to be the ultimate dimerization products of arylsulfinyl radicals.[22]) Furthermore, the observation of **7** and **8** eliminates heterolytic cleavage. The "cross sulfoxides" observed in acetonitrile in the double label experiments also support the formation of free radicals, as does the result that optical rotation is lost faster than starting material, even in viscous solvent. Finally, Wagner and coworkers have shown that the sulfinyl group is an excellent "radical leaving group." Rate constants for loss of RSO$^•$ are faster than those of Br$^•$ in certain reactions.[23-25] For these reasons, we believe that simple α-cleavage and reclosure is the best explanation for the formation of **2**.[26]

As pointed out before, reactions rationalized by formation of sulfenic esters represent only a subset of those which are best explained by α-cleavage.[16,27-33] The best structural correlation that can be drawn for separating the sulfoxides which appear to form sulfenic esters from those which do not is simply the availability of an alternative favorable reaction pathway for the putative radical pair or biradical. In the present case, the "alternative pathway" is diffusive separation. The result of the competition between separation and geminate recombination depends substantially on viscosity of the solvent, consistent with our observations.

Reactive State Multiplicity. We assign the reactive state of **1** to be singlet based both on the very high yield of **2**, which represents geminate recombination, and the

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(26) There is another conceivable mechanism by which chirality of 1 might be lost. This is a rapidly reversible, photoinduced, [2,3] sigmatropic rearrangement analogous to that observed for the interconversion of allylic sulfoxides and sulfenic esters. This rearrangement is negligible in the ground state for **1**. Neither have we any evidence that it occurs in the excited state, such as products containing an *o*-methylphenoxy moiety. Moreover, it cannot account for the overwhelming majority of products, derived from the α-cleavage step, which occurs with quantum yields of 0.4–0.5 (see text). Formally, this process cannot be ruled out, but it would have to be a process in addition to the major α-cleavage pathway.

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sharp contrast that is drawn between photolysis in acetone and other solvents. The cage effect is nearly 100% in 2-methyl-2-propanol, and a significant cage effect is observed even in acetonitrile, which has quite a low viscosity. By contrast, in acetone, much larger proportions of the escape products **7** and **8** are observed, though the viscosities of acetone and acetonitrile are within 5% at room temperature. Because the sulfenic ester is not directly observed (*vide infra*), a cage effect cannot be calculated, but it is certainly very small. Also, $\Phi_{\mathrm{rot.}}$ is much closer to Φ_{loss} in acetone than in acetonitrile. This can be interpreted to mean that a smaller percentage of molecules which cleave undergo geminate recombination, which is consistent with triplet reaction in acetone and singlet cleavage otherwise. However, we certainly cannot rule out a mixture of singlet and triplet cleavage. Though it was observed that Φ_{loss} is not decreased by the presence of O_2, we were not able to carry out any other meaningful triplet quenching experiments (*e.g.*, addition of isoprene) because the high energy wavelengths necessary for selective photolysis of **1** are also absorbed by the quenchers.

There is a second significant observation regarding the photolysis of **1b** in acetone, the absence of sulfenic ester **2b**. We hypothesize that triplet energy transfer from acetone to **1b** may be endothermic by as much as 2–3 kcal/mol, given the triplet energies of related sulfoxides, and thus relatively slow.[13] (Self-quenching by acetone is almost insignificant.[34]) On the other hand, the absorption spectrum of **2b** makes it self-evident that energy transfer from acetone (E_T = *ca.* 79 kcal/mol) would be substantially exothermic, and likely near the diffusion-controlled limit. Under those circumstances, any sulfenic ester which had been formed might be selectively destroyed by sensitization with acetone. We checked this idea by photolyzing solutions containing both **1b** and **2b** in acetone. The starting concentration of each compound was 4–5 mM. The concentrations of both materials were monitored as a function of photolysis time until **2b** was about 30% consumed. Within experimental error, the concentration of sulfoxide was identical to its original value.

Quantum Yield of α-Cleavage. If the excited states of **1** were racemic or had a very low barrier for inversion, we would expect the quantum yield for loss of optical activity, $\Phi_{\mathrm{rot.}}$, to be approximately unity. As the observed values of $\Phi_{\mathrm{rot.}}$ are significantly less than 1, we assume that loss of optical activity occurs at a later stage. The most reasonable hypothesis is that stereochemistry is lost in radical pair **12**. When **12** recombines, it may form the sulfenic ester **2** or may return to starting material **1**, with at least partial racemization. Therefore, we may use the observed values of $\Phi_{\mathrm{rot.}}$ and Φ_{loss} to estimate the quantum yield of α-cleavage. The difference between $\Phi_{\mathrm{rot.}}$ and Φ_{loss} for (*S*)-**1b** is attributed to sulfinyl-benzyl radical pairs **12** which reverted to **1b**.[26] If we assume that the initial cleavage produces a radical pair which has an equal probability of forming (*S*)- or (*R*)-sulfoxide on recombination, then $\Phi_{\mathrm{rot.}}$ is identically the quantum yield for cleavage, Φ_{cleave}.

$$\Phi_{\mathrm{inv}} = (\Phi_{\mathrm{rot.}} - \Phi_{\mathrm{loss}})/2$$

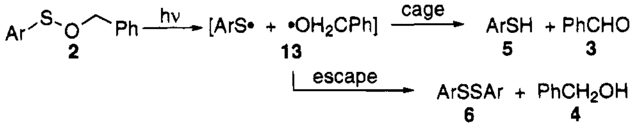
$$\Phi_{\mathrm{cleave}} = \Phi_{\mathrm{loss}} + 2\Phi_{\mathrm{inv}} = \Phi_{\mathrm{rot.}}$$

Because the reversion of **12** is a geminate process of a singlet radical pair, there may actually be a preference for returning to the original enantiomer. Therefore, the actual Φ_{cleave} may be somewhat higher than $\Phi_{\mathrm{rot.}}$.

$$\Phi_{\mathrm{cleave}} \geq \Phi_{\mathrm{rot.}} > \Phi_{\mathrm{loss}}$$

The observed value of $\Phi_{\mathrm{rot.}} = 0.42$ in 2-methyl-2-propanol is thus assigned as the lower limit for Φ_{cleave} of **1b** in that solvent. Of course, this analysis is only valid for low conversions, where photolysis of (*R*)-sulfoxide and **2b** are negligible. An interesting, but not surprising, conclusion which can be drawn is that regioselectivity of recombination by radical pair **12** is clearly kinetically controlled by an early transition state, given that the sulfoxide/sulfenate equilibrium generally lies quite far to the side of the sulfoxide.

Photolysis of Benzyl Arenesulfenic Esters. Photolysis of sulfenic esters **2** yields no detectable amount of the corresponding sulfoxides **1**. As the optical rotation results indicate that the sulfinyl–benzyl radical pair undergoes a partitioning between formation of sulfenic esters and sulfoxides, it can be concluded that cleavage of the S–O bond is strongly favored over cleavage of the O–CH_2 bond which would yield the original radical pair **12**. Products arise from disproportionation of radical pair **13** or reactions of the solvent-separated radicals. Any accumulated **5** may act as an active hydrogen atom donor for escaped benzyloxy radicals, along with the solvent. Formation of **6** is thus compounded by reactions of **5** with radicals and probably small amounts of other oxidizing species in solution. Though our photolyses were carried out under anaerobic conditions (Ar flushing), the analyses were not, and some **5** may have converted to **6** at that point as well.



Photolysis of **1b** at 300 nm in the solid state provides an example of *in situ* preparation of **2**, followed by its selective photolysis under conditions where the cage effect was expected to be quite high, due to limited mobility of the intermediates. The observed product ratios in these cases are within experimental error of a 1:1 ratio of "benzyl" and "sulfinyl" products, represented by **3** and **5** + **6**. We take the small quantity of **6** to be an artifact of subsequent oxidation during handling.

The assignment of the multiplicity of the reactive state of **2** is less definite than for **1**. The substantial dependence of the percentage of "cage" products (benzaldehyde and arenethiols) on the viscosity of solvent are suggestive of a triplet radical pair, but by no means is this conclusive. In particular, it is expected that the thiyl–alkoxyl radical pair **13** would undergo very rapid intersystem crossing due to strong spin-orbit coupling, so ordinary criteria based on products are not likely to be useful. Pasto has recently studied the photolysis of various alkyl *p-nitro*benzene sulfenates[11,35–38] and has concluded that

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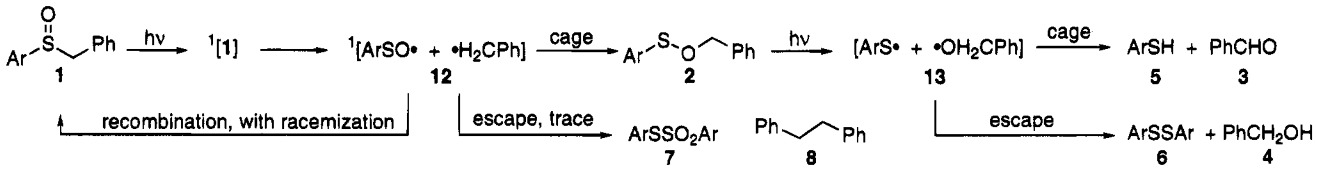

Figure 6. Proposed overall reaction scheme for photolysis of **1**.

the chemistry is triplet-based. While this is quite possibly true here as well, it should be recognized that the nitro group is a strong perturbation on the chromophore which also has important effects on the observed chemistry.

	PhSO• +	PhCH$_2$•	$\leftarrow$ **2a** $\rightarrow$	PhS• +	PhCH$_2$O•
ΔH_f, kcal/mol	13	49.0		54.9	28.1

A further point of interest regarding the photochemistry of **2** is that the selectivity for S−O bond cleavage over O−CH$_2$ cleavage is a slight surprise, given the energetics. The heats of formation of phenylsulfinyl,[39] benzyl,[40] phenylthiyl,[40] and phenylmethoxyl[41] are all either experimentally known or can be reliably estimated to within a few kcal/mol by Benson additivity methods.[42] Given these values, the radical pair **12** is more stable than **13** by about 20 kcal/mol! While this case appears to be strongly biased by the benzyl group, the result is similar with an unbiased system. The heats of formation of all the relevant species are known for homolysis of methyl methanesulfenate by either S−O or O−CH$_3$ cleavage[39,40,43] and the latter is thermochemically favored by about 17 kcal/mol. Despite this, it is known that photolysis of *tert*-butyl methanesulfenate also proceeds by S−O cleavage.[44] *Ab initio* computations at the MP2/6-31G(d,p)//RHF/6-31G(d,p) level indicate that the HOMO of methyl methanesulfenate resides largely on S, but is π-antibonding on both S−CH$_3$ and S−O. The LUMO is more complex, but is clearly σ-antibonding along S−O, but not S−CH$_3$. The similarity between the simple alkyl cases and the aryl sulfenate used here is notable because the character of the chromophore is strongly perturbed by the aryl group, in that the lowest energy absorption band for the alkyl case has λ_{max} about 265 nm.[44]

Summary

The data presented in this paper make a very strong case that the photolysis of aryl benzyl sulfoxides proceeds through the mechanism outlined in Figure 6. The primary process is cleavage of the S−CH$_2$ bond by **1** in an excited singlet state. The assignment of multiplicity is based on high cage effects and dramatic differences in product distribution when the reaction is acetone sensitized. When the photolysis of **1** is carried out using well-chosen wavelengths (*i.e.*, <280 nm) and solvents (*e.g.*, 2-methyl-2-propanol), **2** and **1** with inversion of configuration at sulfur are the nearly exclusive products up to reasonable conversion. Using longer wavelength light results in selective photolysis of **2** so that other products (*i.e.*, **3**−**6**) *appear* to be primary. Because of effects of viscosity and the wavelength dependence of secondary photolysis, quantitative descriptions of product distributions at high conversion are not reliable, but **1** is converted quantitatively to **2** at modest conversion in 2-methyl-2-propanol. On the basis of disappearance of **1b** and its partial racemization, quantum yields for the cleavage of **1b** and its conversion to **2** in 2-methyl-2-propanol are estimated at ≥0.42 and 0.21, respectively.

Photolysis of **2** proceeds through S−O bond cleavage to yield arenethiyl and alkoxyl radicals. Disproportionation of the radical pair **13** yields **3** and **5**. By conducting the photolysis in the solid phase, where radical mobility is strongly limited, these are nearly the exclusive products. In solution, products corresponding to escape from and recombination in the geminal cage are quite competitive.

In sum, the photolysis of **1** follows the previously proposed sulfoxide → sulfenate → products pathway,[1] but this is the first case in which that has been rigorously established and the first case in which an acyclic sulfoxide has been shown to conform to this path. It is shown that the sulfenic ester plays no part in racemization in this case, as photolysis of **2** does not form **1**. Racemization is believed to result from recombination of the geminate radical pair which partitions between formation of **2** and reversion to (racemic) **1**. Further studies into the structural parameters which favor this course of reactivity over others in sulfoxide photochemistry are ongoing.

Experimental Section

General Methods. Except as noted, spectro grade solvents were used as received for all photolyses. 2-Methyl-2-propanol was reagent grade, but did not contain significant light-absorbing impurities. A small quantity of water (1% by volume) was added. Melting points were uncorrected. NMR spectra were obtained on a Varian VXR-300 spectrometer. GC−MS data were obtained using a VG Magnum ion trap instrument. Other GC data were obtained with a HP 5890 Series II gas chromatograph equipped with an FID detector and a 10 m HP-1 column. Optical rotation was monitored using a DIP-370 digital polarimeter (Japan Spectroscopic Co.), with precision of ±0.001°. HPLC data were collected with a HP 1050 liquid chromatograph with a diode array detector. A 25 cm C-18 reversed phase 3 mM column was used. Elutions were with acetonitrile/water gradients. Response factors were determined against internal standards for GC and HPLC for each compound quantified. The estimated error of the response factors is about ±10%.

Compounds. Racemic sulfoxides **1a**−**d** were prepared by oxidation of the corresponding sulfides, derived from the arenethiolate and benzyl bromide (or *p*-methylbenzyl bromide), with H$_2$O$_2$ in methanol.[45,46] Phosphorescence spectra were obtained as described previously.[13] (+)Benzyl *p*-tolyl sulfoxide

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was prepared by reaction of benzylmagnesium bromide with the corresponding menthyl sulfinate.[19,45,47,48] Only sulfoxide **1c** was previously unknown: mp 99–100°; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.96 (d, 1H, J = 12.6 Hz), 4.07 (d, 1H, J = 12.6 Hz), 6.87 (d, 2H, J = 8.1 Hz), 7.06 (d, 2H, J = 8.1 Hz), 7.35–7.50 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 63.3, 124.3, 126.0, 128.7, 129.1, 130.2, 131.0, 138.0, 142.9; IR (KBr, cm^{-1}) 1032, 754, 735, 687.

Sulfenates **2a** and **2b** were prepared by reaction of benzyl alcohol (or *p*-methylbenzyl alcohol) with the corresponding sulfenyl chloride.[19] After crude workup the compounds were approximately 90% pure as determined by NMR; the major impurity was phenyl disulfide or tolyl disulfide, as appropriate. Vacuum distillation, in our hands, did not affect the total purity. We were unable to find preparative chromatographic conditions which did not result in decomposition of the sulfenic esters as well. Finally, the 90% pure materials were used and "background" impurities were subtracted from the data collected in their photolysis. The UV observed with the 90% pure samples closely matched that of the isolated sulfenate peaks in the HPLC traces.

Product Identifications. Product identification was based on comparison to genuine samples in chromatographic behavior.[48,49] GC–MS data and HPLC-derived UV spectra were obtained. Once products were established, correspondence between retention times for experimental and genuine samples was reverified for any change of chromatographic conditions. ^{1}H NMR data were used for some of the initial, high conversion experiments. Only sulfenic esters **2c** and **2d** were neither fully characterized nor commercial compounds. These materials were prepared the same way as sulfenates **2a** and **2b**, but were only characterized by retention times on HPLC and the UV/vis spectrum so obtained. All four sulfenic esters had very similar HPLC retention times and nearly identical UV/vis spectra.

Photolyses. Unless otherwise indicated, photolyses were carried out using a 150 W Xe lamp and monochromator setup from Photon Technologies, Inc. The linear dispersion of the monochromator is 4 nm/mm, and photolyses were carried out with slit widths of 6 mm. The cells for these photolyses were standard 1 cm quartz cells, which are positioned exactly at the exit of the monochromator so that all of the exiting light hits the sample. All solution photolyses were carried out with magnetic stirring and after Ar flushing to remove O_2. As noted, photolyses were carried out using an RMR-500 "mini-Rayonet" from Southern New England Ultraviolet. The 300 nm bulbs, which emit a broad band centered about 300 nm, were used. The photoreactor has been modified so as to have both magnetic stirring and a cooling fan, which keeps the sample at ambient temperature. Unless otherwise noted, starting concentrations of 3–6 mM were used.

Solid Photolyses. Experiments were carried out in two fashions. First, approximately 10 mg of **1b** was dissolved in methylene chloride. This solution was used to coat the inside of a quartz 5 mm NMR tube with the solid material then blanketed with Ar under a septum. This NMR tube was immersed in a bath of liquid nitrogen inside a Suprasil Dewar with transparent sides ordinarily used for EPR and phosphorescence measurements. The Dewar was positioned inside the Rayonet described above and photolyzed for 1 h with 300 nm bulbs. The tubes were allowed to come to room temperature. The solid was dissolved in acetonitrile and analyzed by HPLC. Conversion was about 10%. Benzaldehyde, *p*-thiocresol, and *p*-tolyl disulfide were observed in a ratio of 1.0:0.9:0.1.

A 100:1 mixture of IR-grade KBr and **1b** was prepared as a pellet as for an IR measurement. This pellet was transferred to a quartz test tube and blanketed with Ar under a septum. The pellet was irradiated in the Rayonet with 300 nm bulbs for 1 h. The pellet was crushed and washed several times with acetonitrile. The resulting solution was analyzed by HPLC. Conversion was about 5%. Benzaldehyde, *p*-thiocresol, and *p*-tolyl disulfide were observed in a ratio of 1.0:0.85:0.1.

Quantum Yields. Quantum yields were determined using the PTI lamp. The actinometer was azoxybenzene.[50] Quantification was done with UV, GC, and HPLC. Hexadecane and *p*-xylene were used as internal standards for GC and HPLC, respectively. Sample and actinometer cells were sequentially irradiated. The actinometer cells were used to determine the photon flux, which was then used to convert the rate of loss of the material of interest into a quantum yield. All quantum yields were determined from solutions that began at concentrations of 3–5 mM, and conversions were kept under 10%. Several of the measurements were done with both GC and HPLC detection. The values determined by these different methods varied by no more than about 15%, consistent with repetitive measurements using the same method.

Computations. Computations were done using Spartan 3.1.[51] Full geometry optimization was used at the RHF/6-31G(d,p) level, and MP2 correction was done at this geometry. Starting geometries with both gauche-like and anti-like conformations converged to a single conformation with a C–S–O–C dihedral angle of 92°. Other geometrical parameters: C–S–O angle 100.5°, S–O–C bond angle 116.1°, C–S bond length 1.80 Å, S–O bond length 1.65 Å, O–C bond length 1.41 Å.

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