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Photolysis of Alkyl Aryl Sulfoxides: α-Cleavage, Hydrogen Abstraction, and Racemization[1]

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The photochemistry of a series of alkyl aryl sulfoxides is described. The initial event of the photolysis process is homolytic cleavage to form sulfinyl/alkyl radical pairs. The radical pair partitions between recombination to starting material, formation of sulfenic esters, disproportionation to an olefin and benzenesulfenic acid, and formation of typical radical escape products. The quantum yield for conversion depends on the structure or the reactivity of the alkyl radical, with the sequence benzyl > tertiary alkyl > secondary alkyl > primary alkyl > (di)aryl. The high racemization efficiency of some aryl primary-alkyl sulfoxides suggests that another nonradical pathway for the photoracemization process may exist. Product analysis does not support any hydrogen abstraction pathways.

Introduction

A common mechanistic assumption in the photochemistry of sulfoxides is a reaction pathway that begins with homolytic cleavage of a C−S bond, or α-cleavage.[2,3] Although most of the observed products involve secondary photochemistry, relatively unstable primary photoproducts such as sultenes (cyclic sulfenic esters) and sulfines (ketene analogs) have been isolated in a few cases.[4−8] Despite good evidence for the α-cleavage process, little is known about the structural requirements for this reaction.

We recently reported the photochemistry of aryl benzyl sulfoxides **1**.[9] Most of the previous sulfoxide substrates had been cyclic or carbonyl-containing structures, and we felt it desirable to use a simple acyclic test case to ensure that the chemistry was completely consistent with C−S homolysis. Compound **1** was viewed as a prototypical choice, a molecule that would have high susceptibility to α-cleavage and for which regiochemistry was easily predictable. In solvents of low viscosity, radical "escape" products (diarylethanes and thiosulfonates) were observed, and in no solvents were products attributable to heterolytic cleavage trapped. In higher viscosity media, virtually all of the radical pairs could be shunted to the expected "cage" products: the original sulfoxide and the sulfenic ester **2**. The proposed mechanistic scheme, which indeed included sulfoxide α-cleavage, is illustrated in Figure 1.

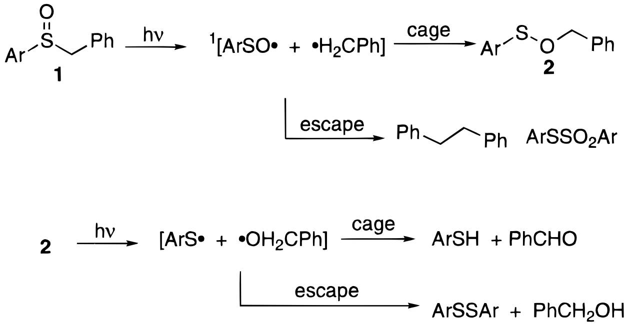
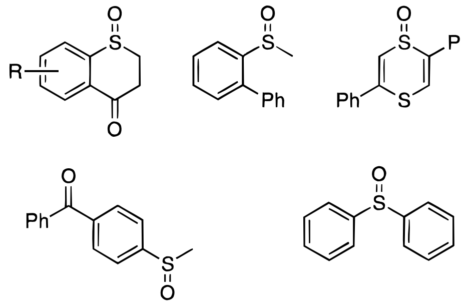


Figure 1. Proposed photolysis mechanism of aryl benzyl sulfoxides.

Chart 1



However, α-cleavage has been invoked for much less favorable structure types than **1**. Chart 1 illustrates a few examples in which less than ideal radicals would be produced on C−S homolysis.[2,8,10−18] If correct, these examples point out that the sulfoxide is significantly more susceptible to photochemical α-cleavage than its carbonyl analog.

Here we report an examination of the effect of molecular structure on the proclivity of the compound for

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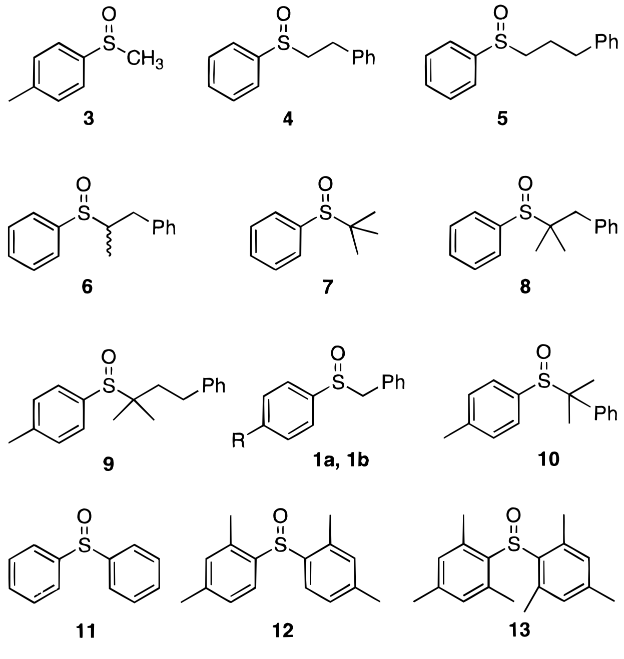
Chart 2



α-cleavage and the selectivity of that cleavage for either C−S bond. In each case, one of the substituents is an aryl group: phenyl or *p*-tolyl. The other substituent is primary, secondary, tertiary, benzyl, or aryl but is remotely labeled with a phenyl group for ease of detection.

Among the issues addressed is the quantum efficiency for reaction as a function of alkyl substituent. We show that the quantum yield for chemical conversion qualitatively follows the radical stability. It is confirmed that even diaryl sulfoxides are susceptible to α-cleavage. The observation of olefin formation from the photolysis of a number of the sulfoxides reveals a previously unreported disproportionation pathway for the initial radical pair.

Two other significant issues are addressed. First is the matter of hydrogen abstraction by sulfoxides. Over the years, certain transformations have been rationalized by invoking internal hydrogen abstraction in analogy to carbonyl chemistry. However, the evidence for such processes is scant compared to that now available for α-cleavage. Among the present compounds, a few might have been expected to be favorable hydrogen abstraction candidates. However, no products which could be unequivocally assigned to hydrogen abstraction were observed.

Finally, there is the matter of photochemical stereomutation of sulfoxides. As we and others have pointed out, this reaction is plausibly explained as a result of α-cleavage and recombination with randomization of stereochemistry. However, others have suggested that a simple inversion of the sulfur center is responsible for observed stereomutations. We find two compounds whose quantum yield of stereomutation is more than 1 order of magnitude higher than that for chemical conversion and conclude that a stereomutation mechanism which does not involve radical intermediates is likely.

Results and Discussion

The compounds used in the study, all of which have a phenyl or *p*-tolyl substituent, are illustrated in Chart 2. As the second carbon substituent, compounds **3**−**5** have a primary alkyl group. Compounds **4** and **5** were used because of the well-known quenching of ketones by β-phenyl groups[19] and to give both β- and γ- positions the optimal position for internal hydrogen abstraction. (β-Abstraction has been proposed more often than γ-abstraction for sulfoxides.[2,3]) Compound **6**, which has a secondary alkyl group, was used as a mixture of diastereomers due to difficulty in separation. Compounds **7**−**9** have tertiary alkyl groups, while **1** and **10** have benzyl groups. Diaryl sulfoxides are represented with compounds **11**−**13**.

1. Photolysis Products and Quantum Yields. Photolysis of the sulfoxides in Chart 2 until completely consumed creates complex reaction mixtures. Because secondary photolysis of some of the products is a significant problem, the composition of the mixture depends on the irradiation wavelength and the extent of photolysis. Viscosity is another important experimental parameter, since radical pairs are generated. Additional complexity is lent by the thermal chemistry of the sulfenic acids and esters that are produced as primary products.[20] Sulfenic acids condense to thiosulfinic esters, which in turn disproportionate to disulfides and thiosulfonates. Hydrolysis affords sulfinic and sulfonic acids. We also find that photolysis of the arenethiosulfonates provides sulfinic and sulfonic acids, along with disulfide. All of these sulfur derivatives are detectable after longer photolysis periods.

Unfortunately, the secondary chemistry problem is generally worse for compounds **3**−**10** than it was for **1**. To keep it to a minimum, the product yields reported here are measured at ≤10% conversion. Starting concentrations for solution work were all 3−5 mM. As previously,[9] the solvent of choice was 2-methyl-2-propanol, spiked with 1% H_2O to prevent freezing. Sulfenic esters from photolysis of **4**−**10** have similar absorption spectra as those from aryl benzyl sulfoxides and can be particularly susceptible to secondary photolysis at lower energy wavelengths, having higher extinction coefficients than the sulfoxides.[9] Thus, photolysis was carried out well into the sulfoxide absorption band, at 267 nm. Although alkyl esters of benzenesulfenic acid are thermally labile,[21] they are sufficiently stable for reverse-phase HPLC detection.

The photolysis products obtained at modest conversions are reported in Table 1. Each of the sulfoxides was photolyzed to similar conversions on multiple occasions, but the entries in the table are for representative single runs. The errors in the reported yields are in the range of ±15% of the reported value. Individual response factors were obtained for all products, with the exception of the sulfenic esters. The response factor for benzyl benzenesulfenate (**2**) was used for all sulfenic esters, as they were very difficult to obtain in sufficient purity for response factor determination. This approximation was justified on the basis that **2** contains the same spectral and structural features as all the other sulfenic esters of interest, but it may introduce an uncertainty in their quantification.

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Table 1. Photolysis Products and Yields for Photolysis of Sulfoxides to ≤10% Conversion

			mass balance	
compd	solvent	products (yield, in %)[a]	aryl	alkyl
4	*t*-BuOH	sulfenate[b] (24), PhC_2H_5 (18), $PhCH{=}CH_2$ (8), C_6H_6 (22), PhOH (25[c]), $PhSO_2SPh$ (8), $PhSSCH_2CH_2Ph$ (6), PhSSPh (5)	see text	see text
4	CH_3CN	PhC_2H_5 (57), $PhOH/PhCH_2CH_2OH$ (36[c]), C_6H_6 (19), sulfenate (13), $PhSO_2SPh$ (12), $PhSCH_2CH_2Ph$ (10), PhSSPh (8), $PhSSCH_2CH_2Ph$ (8)	see text	see text
4	acetone	PhC_2H_5 (33), PhCHO (15), $PhSO_2SPh$ (8), $PhSCH_2CH_2Ph$ (7), C_6H_6 (7), $(PhCH_2CH_2)_2$ (6), $PhCH{=}CH_2$ (5), PhSSPh (2), PhPh (1)	36	72[e]
5	*t*-BuOH	PhC_3H_7 (34), sulfenate (18), PhOH (22), C_6H_6 (15), $PhCH_2CH{=}CH_2$ (12), $PhSO_2SPh$ (4), $PhSS(CH_2)_3Ph$ (4), PhSSPh (3)	73	68
5	CH_3CN	PhC_3H_7 (52), PhOH (21), $Ph(CH_2)_3OH$ (15), C_6H_6 (9), $PhSS(CH_2)_3Ph$ (6), $PhS(CH_2)_3Ph$ (5), $(Ph(CH_2)_3S)_2$ (3), PhSSPh (4), $PhCH_2CH{=}CH_2$ (4), sulfenate (trace)	49	88
5	acetone	PhC_3H_7 (26), $Ph(CH_2)_3OH$ (11), C_6H_6 (7), $PhCH_2CH{=}CH_2$ (4), $(Ph(CH_2)_3)_2$ (4), $PhS(CH_2)_3Ph$ (3), $PhSO_2SPh$ (5), PhSSPh (1)	22	52
6	*t*-BuOH	sulfenate (51), $PhCH_2CH{=}CH_2$ (22), $PhCH{=}CHCH_3$ (17), PhCHO (7), PhC_3H_7 (6), $PhCH_2C(O)CH_3$ (6), PhSSPh (4)	59	109[e]
8	*t*-BuOH	sulfenate (41), $PhCH_2C(Me){=}CH_2$ (33), $PhCH{=}CMe_2$ (11), PhS(O)SPh (10), PhCHO (3), PhSSPh (2)	65	88[e]
9[d]	*t*-BuOH	sulfenate (30), $PhCH_2CH_2C(Me){=}CH_2$ (40), ArS(O)SAr (11), $PhCH_2CHC{=}CMe_2$ (4), ArSSAr (2)	56	74
10[d]	*t*-BuOH	sulfenate (80), $PhC(Me){=}CH_2$ (22), ArSS(O)Ar (4), ArSSAr (3)	94	102

[a] Relative to consumed starting material. [b] In this and all subsequent cases, the sulfenic ester refers to the isomer of the starting sulfoxide corresponding to alkyl−S cleavage and recombination. [c] These two compounds could not be separated. Phenol was positively identified from its low energy UV absorption band, but the ratio of the two compounds could not be determined. [d] "Ar" refers to *p*-tolyl in the list of products. [e] This includes benzaldehyde.

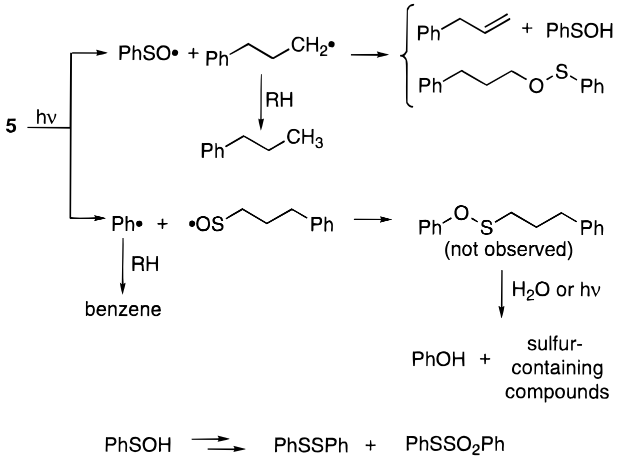

Figure 2. An α-cleavage scheme to account for the products of photolysis of **5**.

Given that α-cleavage is the dominant chemistry, one can construct mass balances for the "aryl half" and the "alkyl half" of these molecules. For all but **4** and **5**, the aryl half also corresponds to the sulfur-containing half. Usually, better mass balances are observed for the alkyl fraction of the molecules than for the aryl (sulfur) portion. A few mass balances slightly over 100% are probably associated with errors in the sulfenic ester response factors. For the chemistry of **4** only, there is an ambiguity due to our inability to separate phenol and 2-phenylethanol using the same column and HPLC solvents as for all the other compounds. The UV spectra of the peak clearly indicated the presence of phenol, but the fraction of the peak which was due to 2-phenylethanol was not determined.

The products in Table 1 are consistent with α-cleavage schemes analogous to Figure 1. A representative scheme for compound **5** is shown as Figure 2. Minor amounts of the deoxygenation product were observed on acetone-sensitized photolysis of **4** and **5**.[22] Only benzaldehyde, which is a component of the mixture for **4**, **6**, and **8**, is unaccounted for using schemes like Figure 2. This is discussed further in the section on internal hydrogen abstraction.

The solvent effects, reported explicitly for **4** and **5**, were consistent with those previously reported for **1**.[9] In comparison to 2-methyl-2-propanol, use of acetonitrile affords a greater percentage of radical "escape" products. The viscosity of acetone and acetonitrile are similar, but the former is used as a triplet sensitizer. Acetonitrile is somewhat more polar than acetone,[23] but this was not thought to be significant for purposes of this experiment. The triplet energies for these sulfoxides are expected to be of the order of 80 kcal/mol,[24] and a high-energy sensitizer is necessary. In the photolysis of **1**, the contrast of product distributions from direct photolysis in acetonitrile and sensitized photolysis in acetone was sufficiently dramatic that it was concluded that the reactive excited state was a singlet.[9] Here, the results are more ambiguous, and we hesitate to make any assignment about the spin of the reactive excited state. Diene and oxygen-quenching experiments were also ambiguous, only leading us to conclude that a long-lived triplet is not likely involved.

Several salient points can be derived from the data in Table 1. First among these is that the reaction mixtures derived from the primary compounds **4** and **5** are qualitatively more complex than those of the sulfoxides **6**−**10**. A closer inspection reveals that the "extra" products appear to derive from phenyl−S cleavage, as illustrated in Figure 2. For **4**, these consist of benzene, $PhSSCH_2CH_2Ph$, and phenol. The sulfenic ester $PhOSCH_2CH_2Ph$ was not detected. In fact, efforts to obtain it by independent synthesis by the usual route[9] and characterize it by HPLC were unsuccessful, perhaps due to its lability.

In contrast to the primary sulfoxides **4** and **5**, compounds **1** and **6**−**10** did not generate any significant products attributable to aryl−S cleavage. Selectivity for alkyl cleavage is completely restored if the alkyl group is secondary, tertiary, or benzyl.

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

	quantum yield of disappearance, Φ_{loss}	
compd	*t*-BuOH	CH_3CN
3	0.038	
4	0.037	0.052
5	0.039	0.054
6	0.072	
7	0.13	
8	0.10	0.15
9	0.10	
1	0.20	0.28
10	0.25	0.49
11	0.034	
12	0.028	
13	0.012	

[a] All solutions were originally 3−5 mM in starting material and were Ar flushed to remove oxygen. Under these conditions, all of the light is absorbed.

Quantum yields for disappearance of starting material (*i.e.*, all reaction pathways not returning to starting material, Φ_{loss}) were measured for the series of sulfoxides, and they are shown in Table 2. All compounds were 3−5 mM in initial concentration in the various solvents, and the measurements were carried out to conversions ≤10%. All values are averages from multiple runs and had reproducibility within 10%. Apparent quantum yields in acetone (not shown) were generally a little higher than those for direct irradiation. Azoxybenzene was the actinometer, and the wavelength of irradiation was 267 nm.

The data in Table 2 show a monotonic relationship between Φ_{loss} and the stability of the presumed carbon-centered radical for the series of **1** and **3**−**10**, with the value being highest for cumyl, followed by benzyl and then tertiary through primary alkyls. The diaryl sulfoxides also fit into this qualitative relationship. This coincidence is consistent with competition between alkyl and aryl cleavage in **4** and **5**. The photochemistry of **11**[25] is somewhat solvent-dependent[22,26] but is dominated by α-cleavage products, again consistent with this scenario.

While the observed trend itself is not unexpected, what may be somewhat surprising is the similarity in quantum yields shown for the primary (*i.e.*, **4**, **5**) and diaryl (*i.e.*, **11**−**13**) cases. Using Benson-type estimates of the heats of formation of the various isomers of butyl sulfoxides,[27] Benson's estimate for the heat of formation of $PhSO^{\bullet}$,[28] and experimental heats of formations for phenyl and the various butyl isomers,[27] the bond energies for primary-, secondary-, and tertiary-alkyl phenyl sulfoxides are all in the range 56−59 kcal/mol. An estimate of 65 kcal/mol can be made for an aryl C−S bond in **11**. Regardless of the exact bond energies, C−S bond cleavage from the excited state of any of these aromatic sulfoxides is significantly exothermic from either the singlet (E_S ~90−100 kcal/mol) or triplet (E_T ~75−80 kcal/mol) state.

From this data, it cannot be explicitly determined whether the quantum yield trend is due to a trend in the cleavage yield, the efficiency of unproductive recombination, or both. This point was dramatically illustrated by Wagner in his work on the type II chemistry of ketones.[29] Nonetheless, we favor the hypothesis that the quantum yield trend is at least mostly determined by cleavage efficiency. Intuitively, it does not seem likely that high cleavage efficiencies are found throughout and that nonproductive recombination (as opposed to other reactions of the primary radical pair) is very efficient only for the diaryl and aryl primary sulfoxides.

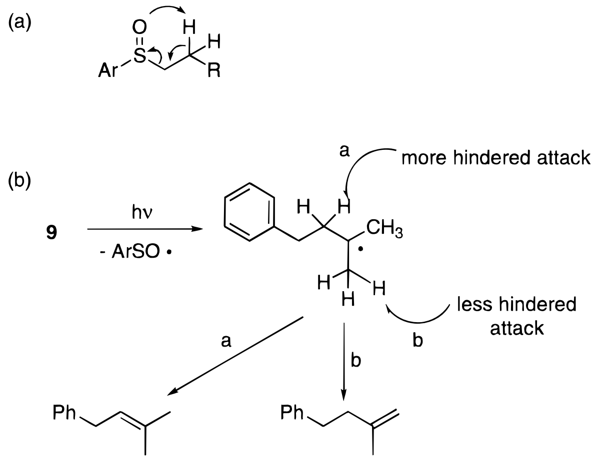

Figure 3. Mechanisms for (a) thermal and (b) photochemical olefin formation.

Table 3. Olefinic Products from Degradation of 6, 8, and 9

compd	conditions	product ratio[a]
		$PhCH{=}CHMe/PhCH_2CH{=}CH_2$[b]
6	*hν*, *t*-BuOH, 267 nm	0.72 (1.1)
	Δ, *t*-BuOH, 80 °C	13 (20)
		$PhCH{=}CMe_2/PhCH_2C(Me){=}CH_2$
8	*hν*, *t*-BuOH, 267 nm	0.18 (0.54)
	Δ, *t*-BuOH, 80 °C	0.63 (1.9)
		$PhCH_2CH{=}CMe_2/PhCH_2CH_2C(Me){=}CH_2$
9	*hν*, *t*-BuOH, 267 nm	0.13 (0.39)
	Δ, *t*-BuOH, 80 °C	0.44 (1.3)

[a] Statistically adjusted selectivity given in parentheses. [b] Sum of *E* and *Z* isomers.

2. Regioselectivity of Alkene Products. From Table 1, it can be seen that alkene products are obtained on photolysis of **4**−**6**, **8**, and **9**. It is proposed that these compounds derive from disproportionation of the initial sulfinyl/alkyl radical pair derived from α-cleavage (*e.g.*, Figure 2). When only one alkene is possible (**4**, **5**), it is the same as is generated thermally in the electrocyclic elimination (Figure 3).[30−33] However, two or more alkenes can be derived from **6**, **8**, and **9**, and their distribution, compared to the thermally derived distributions, supports the α-cleavage/disproportionation hypothesis.

A listing of the relative yields of olefinic products derived from photolysis and thermolysis of **6**, **8**, and **9** is given in Table 3. The selectivity for abstraction of the hydrogen leading to the more stable olefin, adjusted for the number of available hydrogens, is shown in parentheses.

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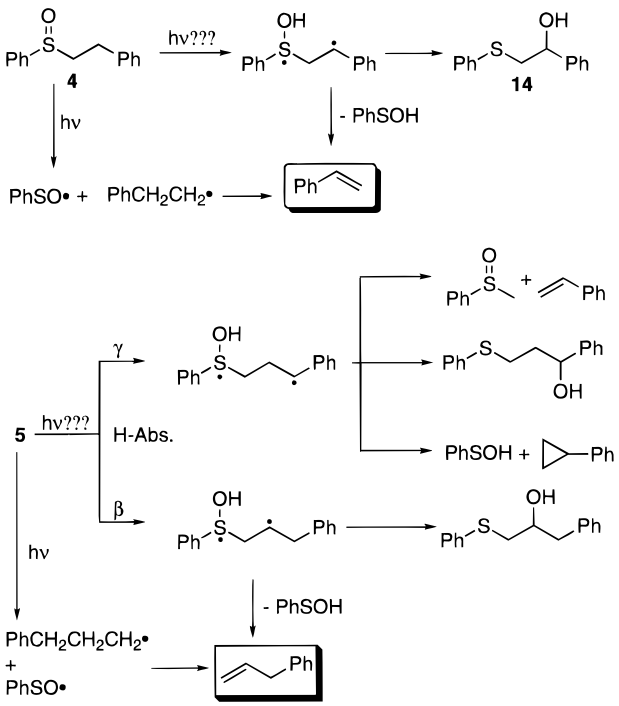


Figure 4. Postulated chemistry of **4** and **5** with hydrogen abstraction as a first step. Only the olefinic products in boxes are observed.

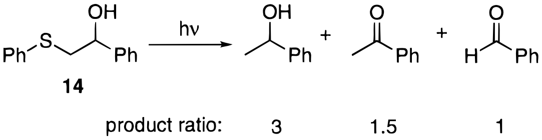
First consider the thermolysis reactions. In each case, the statistically adjusted selectivity favors the more stable alkene isomer. The selectivity is greatest for **6**, for which the choice is a styrene versus a nonconjugated alkene. (It should be recalled that **6** is actually a mixture of diastereomers.) For **8**, this same choice is offered, but the selectivity is lower, presumably for steric reasons. For **9**, the choice is merely between a trisubstituted and disubstituted alkene, and the selectivity approaches 1.

In the photochemical reactions, we presume a radical pair consisting of a sulfinyl and alkyl radical is produced. While the order of weighted selectivities for the more stable alkene is the same, the actual values dip below 1. This is taken as an indication that steric considerations are more dominant in determining which hydrogen will be abstracted in the disproportionation. This is the case because any choice will be highly exothermic and a very early transition state is expected.

3. Intramolecular Hydrogen Abstraction. Compared to the hydrogen abstraction reactions of carbonyls,[29] hydrogen abstraction by sulfoxides is not well established. It has been proposed, however, to account for certain reaction products.[11,34,35] These have been cyclic cases, and abstraction from the β-position is proposed. Alternate pathways can be written for these reactions which instead rely on α-cleavage, followed by olefin formation.[2,3] Subsequent steps are required to achieve the products, though, and alkene-containing sulfenic acids have not been reported in these reaction mixtures.

With **4**, **5**, and the other compounds in hand, an opportunity presents itself to look for products which might unambiguously be attributed to internal hydrogen abstraction (Figure 4). Such products, of course, are a matter of speculation before the experiment. The results of these photolyses, presented in Table 1, do not include any of the speculative products in Figure 4.

Benzaldehyde was a minor product observed for photolysis of **4** (in acetone), **6**, and **8** and is not accounted for by either Figure 2 or Figure 4. All of the compounds for which PhCHO is observed have a benzyl group β to the sulfinyl group. Notably, benzaldehyde was not observed for **5** and **9**, where the benzyl group is γ to the sulfoxide. We therefore thought it was possible (if unlikely, at such low conversions) that benzaldehyde might derive from secondary photolysis of **14** and the corresponding β-hydroxy sulfides from **6** and **8**. Therefore an independent photolysis of **14** was undertaken. With a total quantum yield of 0.15 (same conditions), 1-phenylethanol, acetophenone, and benzaldehyde were all observed, the latter as a comparatively minor product.



Secondary photolysis of **14** and its analogs is therefore viewed as an unlikely source for the benzaldehyde for two reasons. First, in none of the instances when observed was it accompanied by the appropriate alcohol or phenone (*e.g.*, 1-phenylethanol and acetophenone for **4**). Furthermore, while the quantum yield for photolysis of **14** is larger than that of **4**, its UV is unremarkable at the irradiated wavelength. It is extremely unlikely, therefore, that complete conversion of **14** would have taken place at such low conversions of **4**. Unfortunately, we do not have a superior explanation at this juncture.

In principle, the olefin formation observed here can be attributed to β-hydrogen abstraction. If this were so, we might expect a significant difference in the quantum yields for the **3**/**4** and **8**/**9** pairs, because the benzyl position favorable for hydrogen abstraction is a different number of carbons away from the sulfinyl group for each member of the pairs. Instead, nearly identical quantum yields are observed, more consistent with the pairs' identical primary or tertiary natures having influence on α-cleavage. We conclude that the α-cleavage/disproportionation mechanism is much more likely.

Photolysis of *o*-methyl aryl ketones results in formation of transient photoenols. If done in the presence of D_2O or deuterated alcohols, deuterium atoms are incorporated into the methyl group in the reketonization process.[29] In many cases, this technique can be used to convert the CH_3 group to CD_3 nearly quantitatively. An analogous reaction by *o*-methyl sulfoxides could be construed as strong evidence for internal hydrogen abstraction by those compounds. Up to 12 hydrogen atoms might be exchanged in **13** and six in **12**. Sulfoxides **12** and **13** were photolyzed to 30−50% conversion in a mixture of 75% CH_3CN and 25% D_2O. The remaining starting material was examined by GC−MS. There was no evidence of deuterium incorporation, and certainly not of multiple deuterium incorporation. Though negative evidence such as reported here does not and cannot rule out hydrogen abstraction as a primary process of sulfoxide excited states, it undoubtedly contributes to our skepticism.

4. Chiral Sulfoxides and Stereomutation. One of the most important features of sulfoxides is their chirality when substituted with two different groups. The race-

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Table 4. Quantum Yields for Loss of Starting Materials and Optical Activity of Chiral Sulfoxides

	(R)-(+)-**1**	(S)-(−)-**3**	(R)-(+)-**5**
	Φ_{rot} (Φ_{loss})	Φ_{rot} (Φ_{loss})	Φ_{rot} (Φ_{loss})
i-PrOH, 267 nm	0.44 (0.30)	0.90 (0.036)	0.85 (0.037)
t-BuOH, 267 nm	0.42 (0.21)	0.83 (0.038)	0.81 (0.036)
CH_3OH, 267 nm		0.81 (0.054)	
$HOCH_2CH_2OH$, 267 nm		0.80 (0.035)	

mization of sulfoxides under acidic[36] and thermolytic[37-39] conditions has been well studied. On the basis of activation parameters, it was concluded that thermochemical racemization took place by direct inversion of the stereocenter, with the exception of aryl benzyl sulfoxides (*e.g.*, **1**) and allyl sulfoxides. The benzyl compounds were thought to undergo (thermal) α-cleavage and recombination, while the allyl compounds reversibly rearrange to the sulfenic ester.

Photochemical (direct and sensitized) stereomutation is also well-known.[40-48] It has long been recognized that net inversion of the sulfur center could take place directly or through α-cleavage and recombination. Certainly some stereomutation was by the cleavage/recombination mechanism, so the real question is whether an additional mechanism exists.

In our previous photolysis study of **1**, we proposed that cleavage and recombination accounted for loss of optical rotation of solutions of **1** which was in excess of that which could be accounted for by chemical conversion.[9] This was used to determine a quantum yield for α-cleavage. We now report identical experiments carried out with **3** and **5**, whose results are given in Table 4. In the table, Φ_{loss} represents the total quantum yield for chemical conversion taken from Table 2 and Φ_{rot} is the quantum yield for loss of optical rotation. (If there were no mechanisms for racemization at all, Φ_{loss} and Φ_{rot} would be identical.)

Photolysis of chiral sulfoxides in different solvents at 267 nm (concentration = 4−6 mM) shows that the primary alkyl aryl sulfoxides behave quite differently than **1**. Despite the very low values for Φ_{loss}, they have very high values of Φ_{rot}. The comparable values in isopropyl and *tert*-butyl alcohols suggest that external hydrogen abstraction is not important to the stereomutation process. More variation in Φ_{loss} was expected if reversible formation of an achiral sulfuranyl radical had been important. Reversible intramolecular hydrogen abstraction is ruled out by comparable values for **3** and **5**.

The data for **3** and **5** are hypothetically consistent with nearly quantitative cleavage and recombination, accompanied by only very minor amounts of product-generating reactions. We view the latter hypothesis as unlikely. It seems unreasonable that cleavage would be more efficient from **3** and **5** than from **1**, and nearly quantitative besides. Recombination to the sulfoxide would have to be well over 1 order of magnitude faster than either of the other two radical−radical reactions of the radical pair generated from photolysis of **5**. All the radical−radical reactions are extremely exothermic, and the chemical yields of sulfenic ester and olefin are comparable. The photochemical and thermal results for **1** show that it is not inevitable for relatively unhindered radical pairs to form sulfoxides over sulfenic esters with high selectivity. Furthermore, the values of Φ_{rot} for **3** are essentially identical for solvents methanol and ethylene glycol. These two solvents have very similar polarities (dielectric constants within about 15%), but differ in viscosity by more than 1 order of magnitude. This is further evidence against a cleavage−recombination mechanism. Instead, we favor an inversion mechanism for the stereomutation of **3** and **5**. A more detailed conclusion than that cannot be drawn at this time. Efforts continue in our laboratory to clarify this issue.

The racemization of **1** may occur either by a cleavage−recombination mechanism or by inversion. Two points may suggest that **1** may be an exceptional case in which the former is dominant. First, as previously mentioned, the thermolytic racemization is a special case which goes by cleavage and recombination. Second, the singlet nature of the cleavage photochemistry implies that cleavage is very rapid for this compound.

Summary

In this paper, we have presented evidence that α-cleavage is the predominant chemistry for monofunctional alkyl aryl sulfoxides. When the alkyl group is primary, cleavage occurs to a significant extent along both C−S bonds. On the other hand, when the alkyl group is secondary, tertiary, or benzyl, selectivity is high for alkyl−S cleavage. For the first time, alkene products are observed from the disproportionation of the initial radical pair.

Formation of benzaldehyde from **4**, **6**, and **8** is a troublesome result that is not currently explained. However, it appears not to be the result of secondary photochemistry of a β-hydroxy sulfide derived from hydrogen abstraction. In fact, no evidence for product formation from internal hydrogen abstraction is observed.

Racemization of the primary alkyl compounds **3** and **5** occurs with very high quantum efficiency. A cleavage/recombination mechanism cannot be ruled out, but an inversion mechanism is favored.

Experimental Section

General Methods. The photolyses were carried out using a 150 W Xe lamp filtered through a monochrometer with 24 nm linear dispersion. Except as noted, HPLC grade solvents were used as received for all photolyses. 2-Methyl-2-propanol was Fisher Scientific reagent grade, but did not contain significant light-absorbing impurities. It was distilled before use. A small quantity of HPLC quality water (1% by volume) was added in order to insure the alcohol did not freeze. Molecular oxygen was removed from all samples by thorough bubbling with argon.

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Melting points were measured by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. NMR spectra were obtained on a Varian VXR-300 spectrometer. Optical rotation was monitored using a DIP-370 Digital Polarimeter (Japan Spectroscopic Co.) and an Oriel filter (4045 Å, bandwidth 100 Å); precision is ±0.001°. 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. HPLC data were collected with a HP 1050 liquid chromatograph with a diode array detector. An ODS Hypersil reverse phase column (5 μm, 200 × 2.1 mm) was used. Elutions were with acetonitrile/water gradients. Response factors were developed against internal standards for GC and HPLC for each compound quantified. The estimated error of the response factors is about ±10%.

Sulfoxides. (*S*)-(−)-Methyl tolyl sulfoxide **3** (99%, Aldrich) was used as received. Diphenyl sulfoxide **11a** (Aldrich) was recrystallized in hexane before use. The preparations of the aryl benzyl sulfoxides **1**, dixylyl sulfoxide **12**, and dimesityl sulfoxide **13** have been described.[9,24] Phenyl 2-phenylethyl sulfoxide **4**[49] was prepared by hydrogen peroxide oxidation of the corresponding sulfide.[50] *tert*-Butyl phenyl sulfoxide **7** was prepared in 65% yield from *t*-butyllithium and (*S*)-(−)-menthyl benzenesulfinate.[38,51] No attempt was made to assess optical purity.[52]

Aside from their toxicity, thiophenols, used in the preparations below, are severe stench hazards. Extreme care should be exercised that all glassware, gloves, etc., be treated with bleach prior to cleanup or disposal.

(*R*)-(+)-Phenyl 3-Phenylpropyl Sulfoxide (5). This compound was prepared in 40% yield from phenylpropylmagnesium bromide and (*S*)-(−)-menthyl benzenesulfinate.[38,51] Repeated recrystallization from benzene−hexane gave a sample with constant melting point of 53.5−53.8 °C. A racemic sample had melting point of 44−45 °C: ^{1}H NMR ($CDCl_3$) δ 1.95 (m, 1 H), 2.11 (m, 1 H), 2.65−2.85 (m, 4 H), 7.10−7.32 (m, 5 H), 7.45−7.62 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 23.6, 34.6, 56.4, 124.1, 126.3, 128.5, 128.6, 129.3, 131.0, 140.5, 143.9; $[\alpha]^{20}_{405nm} = 0.560$ (c 0.119, 2-propanol), $[\alpha]^{20}_{405nm} = 0.623$ (c 0.120, acetone).

1-Methyl-2-phenylethyl Phenyl Sulfoxide (6). This sulfoxide was prepared in 72% yield as a 1.1:1 mixture of two diastereomers by reaction of Grignard reagent (obtained by reaction of 2-bromo-1-phenylpropane and magnesium) and (*S*)-(−)-menthyl benzenesulfinate in anhydrous ether.[38,51] Separation of this colorless oil on silica gel led to variation of the ratio of diastereomers, but neither pure diastereomer could be obtained, so the original mixture was used. Major product: ^{1}H NMR ($CDCl_3$) δ 1.09 (d, $J = 5.1$ Hz, 3 H), 2.59 (dd, $J =$ 10.2, 7.9 Hz, 1 H), 2.83−2.99 (m, 1 H), 3.09 (dd, $J = 10.2$, 2.7 Hz, 1 H), 7.07−7.68 (m, 10 H). Minor product: ^{1}H NMR ($CDCl_3$) δ 0.99 (d, $J = 5.1$ Hz, 3 H), 2.60 (dd, $J = 10.2$, 7.2 Hz, 1 H), 2.83−2.99 (m, 1 H), 3.29 (dd, $J = 10.2$, 4.5 Hz, 1 H), 7.07−7.68 (m, 10 H). Mixture: ^{13}C NMR ($CDCl_3$) δ 10.2, 12.7, 34.5, 36.6, 60.8, 60.9, 124.7, 125.1, 126.6, 126.7, 128.5, 128.6, 128.9, 129.0, 129.2 (2 overlapped peaks), 130.8, 131.2, 137.7, 138.1, 141.5, 141.7.

1,1-Dimethyl-2-phenylethyl Phenyl Sulfoxide (8). This compound was prepared in quantitative yield by oxidation of the corresponding sulfide using the H_2O_2−urea complex:[53] mp 87−90 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 3 H), 1.06 (s, 3 H), 2.68 (d, $J = 13.1$ Hz, 1 H), 3.01 (d, $J = 13.1$ Hz, 1 H), 7.14−7.32 (m, 5 H), 7.48−7.64 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.3, 20.2, 40.9, 59.4, 126.6, 126.7, 128.1, 128.4, 130.8, 131.2, 135.9, 139.5.

The sulfide was prepared using a slight modification of the method of Ipatieff.[54] 2-Methyl-2-phenyl-2-propanol (40 mmol) and thiophenol (40 mmol) were sequentially added dropwise to a mixture of 8.3 mL of concentrated sulfuric acid and 4 mL of water. After 4 h, the mixture was added to a mixture of ice and ether. After workup and recrystallization from ethanol, a purified yield of 70% was obtained. ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 6 H), 2.89 (s, 2 H), 7.18 (dd, $J = 7.5$ Hz, 1.5 Hz, 2 H), 7.22−7.42 (m, 6 H), 7.58 (dd, $J = 7.5$ Hz, 1.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.1, 49.0, 49.4, 126.5, 127.9, 128.6, 128.9, 130.8, 132.2, 132.8, 132.9.

1,1-Dimethyl-3-phenylpropyl Phenyl Sulfoxide (9). This compound was prepared in the same fashion as **8** in 93% yield: mp 68−71 °C; ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 3 H), 1.19 (s, 3 H), 1.74 (ddd, $J = 14.1$, 12.3, 5.1 Hz, 1 H), 1.97 (ddd, $J =$ 14.1, 12.3, 5.1 Hz, 1 H), 2.40 (s, 3 H), 2.63−2.82 (m, 2 H), 7.16−7.49 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 19.7, 20.1, 21.4, 30.2, 37.6, 58.7, 126.0, 126.4, 128.3, 128.4, 129.1, 136.2, 141.5, 141.6.

The corresponding sulfide was prepared in 82% yield from *p*-thiocresol and 2-methyl-4-phenyl-2-butanol as above: ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 6 H), 1.75 (m, 2 H), 2.34 (s, 3 H), 2.81 (m, 2 H), 7.10−7.30 (m, 5 H), 7.12−7.30 (d, $J = 8.1$ Hz, 2H), 7.43 (d, $J = 8.1$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.2, 28.8, 31.3, 44.1, 48.9, 125.7, 128.3, 128.6, 129.3 (2 overlapping peaks), 137.4, 138.8, 142.5.

1,1-Dimethylbenzyl *p*-Tolyl Sulfoxide (10). This compound was prepared in 87% yield in the same fashion as **8**: ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 3 H), 1.74 (s, 3 H), 2.31(s, 3 H), 6.76 (d, $J = 8.0$ Hz, 2 H), 7.01 (d, $J = 8.0$ Hz, 2 H), 7.18−7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.9, 21.4, 24.2, 63.0, 125.9, 127.6, 128.0, 128.3, 128.6, 130.9, 138.7, 141.2.

The sulfide was prepared from *p*-thiocresol and α-methylstyrene in the same way as the sulfides of **8** and **9**, save that the alkene was used rather than the alcohol in 44% yield: ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 6 H), 2.31 (s, 3H), 6.98−7.44 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 21.2, 29.6, 50.7, 126.4, 126.6, 127.8, 129.0, 136.6, 138.6, 146.5.

Sulfenic Esters. Appropriate sulfenic esters were prepared by reaction of alcohols with benzene- or toluenesulfenyl chloride in the presence of triethylamine.[38] After crude workup, a mixture was obtained that typically contained starting materials, disulfide, and the sulfenic ester (typically ∼50%) as major components. The sulfenic esters were identified by its characteristic UV and retention time behavior. Sufficient purification to get response factors was not generally achievable, so the response factor developed for benzyl benzenesulfenate[9] was used.

Miscellaneous Compounds. Phenyl benzenethiosulfonate and *p*-tolyl *p*-toluenethiosulfonate were prepared by literature methods.[55,56] Phenyl benzenethiosulfinate and *p*-tolyl *p*-toluenethiosulfinate were also prepared by literature methods.[57] The known phenyl 2-phenylethyl disulfide ($PhSSCH_2CH_2Ph$) and phenyl 3-phenylpropyl disulfide ($PhSSCH_2CH_2CH_2Ph$) were prepared by the oxidation of equimolar mixtures of the corresponding thiols.[58] The pure compounds were obtained by silica chromatography of the disulfide mixtures. 1-Phenyl-2-(phenylthio)ethanol[59] and 1-phenyl-3-(phenylthio)-1-propanol[60] were prepared by literature methods.[61] 2-Methyl-4-phenyl-2-butene was obtained from thermolysis of **9**: ^{1}H NMR ($CDCl_3$) δ 1.72 (br s, 3 H), 1.75 (d, $J =$ 1.5 Hz, 3 H), 3.34 (d, $J = 7.2$ Hz, 2 H), 5.33 (t of heptets, $J =$ 7.2 Hz, 1.5 Hz, 1 H), 7.15−7.32 (m, 5 H).

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Product Identifications. Product identification was based on comparison to genuine samples in chromatographic behavior. Except as noted above, compounds were obtained commercially. HPLC-derived UV spectra were obtained and compared. Once products were established, comparison of retention times for experimental and genuine sample were reverified for any change of chromatographic conditions. Some of the alkane and alkene products were also identified by GC−MS.

Quantum Yields. Quantum yields were determined using the PTI lamp. The actinometer was azoxybenzene.[9] Quantification was done with HPLC. *p*-Xylene or 1-phenylundecane was used as internal standards. Sample and actinometer cells were sequentially irradiated and 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%. The data were reproducible from run to run within ±10%, but the absolute error may be somewhat larger than that due to small systematic errors.

Thermolyses. Unless otherwise indicated, thermolyses were carried out using a oil bath with a temperature controller that regulated the temperature within ±0.5 °C of the stated value. In a three-neck flask equipped with condenser and thermometer, a 10 mL solution of the sulfoxide (3−4 mM) containing 1-phenylundecane (Aldrich, 99%) as internal stand was heated at the stated temperature under an argon atmosphere. Small (5 μL) samples were taken out at regular time intervals, and the progress of the reaction was monitored by HPLC. The rates of the reactions were found to fit nicely with first-order decays, and the rate constants were calculated by a least-squares method.

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Supporting Information Available: Chromatograms of **5**, **6**, **8**, and **9** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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