1997

Study on the photolysis and thermolysis of alkyl aryl sulfoxides

Yushen Guo
Iowa State University

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Study on the photolysis and thermolysis of alkyl aryl sulfoxides

By

Yushen Guo

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Organic Chemistry

Major Professor: William S. Jenks

Iowa State University

Ames, Iowa

1997

Graduate College

Iowa State University

This is to certify that the Doctoral dissertation of

Yushen Guo

has met the dissertation requirements of Iowa State University

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Major Professor

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For the Major Program

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For the Graduate College

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ABSTRACT

The sulfoxide, as a sulfur analog of the ketone, is a very important class of organic compounds. It is widely used in organic synthesis, and some are specialty chemicals, such as polymerization initiators and antioxidants. The study of sulfoxide photochemistry started in the early 1960s, but there are still some fundamental questions left unanswered. Generally, there are three proposed primary processes in sulfoxide photochemistry: α-cleavage, stereomutation, and hydrogen abstraction. Sulfoxide deoxygenation is a fourth reaction process. All of these will be discussed in this thesis in various detail.

The thesis begins with a brief deliberation of the objective and justification of this research. Chapter 1 is a general literature review of sulfoxide photochemistry. The following four chapters focus on photolysis and thermolysis mechanism studies of sulfoxides employing various structures. At the end of this thesis is an appendix covering background information on the photochemistry instrumentation used in this research.

The photochemistry of aryl benzyl sulfoxides has been studied in extensive detail as a prototype of α-cleavage. The initial event is homolytic cleavage to form a singlet arylsulfinyl/benzyl radical pair. This radical pair partitions between reversion to starting material with at least partial racemization and closure to form a sulfenic ester. This is the first well characterized sulfenic ester intermediate from the photolysis of acyclic sulfoxides. The assignment of the excited state spin multiplicity is based on high cage effects and a dramatic difference in product distribution when the reaction is acetone sensitized. With acetone sensitization, the primary radical pair undergoes quite significant escape, leading to the formation of diphenyl ethane and aryl arenethiosulfonates. Secondary photolysis of the sulfenic ester leads exclusively to S-O homolysis, yielding the arenethiyl/alkoxyl radical pair from which various isolated products are derived. Quantum yields and other mechanistic observations, including solid state photolysis, are also discussed.

The photochemistry of other alkyl aryl sulfoxides is also described. The initial sulfinyl/alkyl radical pair from homolytic α-cleavage partitions between recombination to starting material, formation of sulfenic esters, disproportionation to alkenes and arenesulfenic acid, and the formation of typical radical escape products. The quantum yield for conversion depends on the structure or the reactivity of the alkyl radical, according to the following order: benzyl > tertiary alkyl > secondary alkyl > primary alkyl > (di-)aryl. The high racemization efficiency of some primary alkyl aryl sulfoxides suggests the possible existence of another non-radical pathway for the photoracemization process. Product analysis does not support any hydrogen abstraction pathways. Absorption spectra and extinction coefficients of phenylsulfinyl radical are determined by nanosecond laser photolysis of several sulfoxides. which provides the strongest evidence for α-cleavage as the predominant primary photochemical process for those compounds.

The last chapter is a comparative thermolysis study of sulfoxides. All thermal reactions in either gas phase or solution display first-order kinetics. The thermal regioselectivity of the alkene products is controlled by the structure of the transition states, which is different from the photochemical process. The mechanism of the high temperature thermolyses shows increasing radical character, along with the classical concerted cyclic elimination mechanism. This is supported by the formation of the alkane products and higher activation parameters. A pulsed stirred-flow reactor was successfully used to study the kinetics of certain less labile sulfoxides. The direct GC injector pyrolysis method has proved to be a simple and fast approach to determine the relative activation parameters of thermolysis products with good precision.

GENERAL INTRODUCTION

Dissertation Organization

This dissertation contains five chapters. Chapter 1 is a general review of the literature on the photochemistry of sulfoxides, which will focus on the α-cleavage reactions, but will also include some hydrogen abstraction and racemization processes. Chapter 2 to Chapter 5 are four independent papers in which some of our results have been published. Chapter 2 discusses the photolysis of aryl benzyl sulfoxides, which focuses on the benzyl phenyl sulfoxide α-cleavage and the function of sulfenic ester intermediates. Chapter 3 pertains to the photolysis of benzyl 2-naphthyl sulfoxide. Chapter 4 contains results of a comparative photolysis study of structurally different sulfoxides, which includes α-cleavage efficiency, racemization, and hydrogen abstraction. The final chapter deals with sulfoxide thermolysis, which includes alkene regioselectivity, temperature effects on the mechanism, pulsed stirred-flow thermolysis, and direct gas chromatograph injector pyrolysis. Following the last paper are general conclusions. At the end of this thesis is an appendix with background information on the photochemistry instrumentation which were employed in the research described in this thesis.

Objectives

The overall goal of the research described in this thesis is to develop a systematic understanding of the photochemistry of aryl alkyl sulfoxides. This includes an exploration of two major proposed mechanisms (α-cleavage and hydrogen abstraction), racemization, intermediates, reactivity-structure relationships, quantum yields, product distributions, and a comparative study of sulfoxide thermochemistry.

Significance

In addition to their fundamental importance as intermediates of sulfide oxidation and as ketone analogs, sulfoxides have been widely used as versatile starting materials for modern organic synthesis. Their chemistry has been widely investigated, and continues to be an exciting area of research.[1-5] As diastereoselective auxiliaries, chiral sulfoxides have been successfully used in the synthesis of various enantiomerically-enriched organic compounds.[6] The synthesis of juvenile hormone II (**5**) is a recent example of the synthetic applications of chiral alkyl aryl sulfoxides (Figure 1).[7]

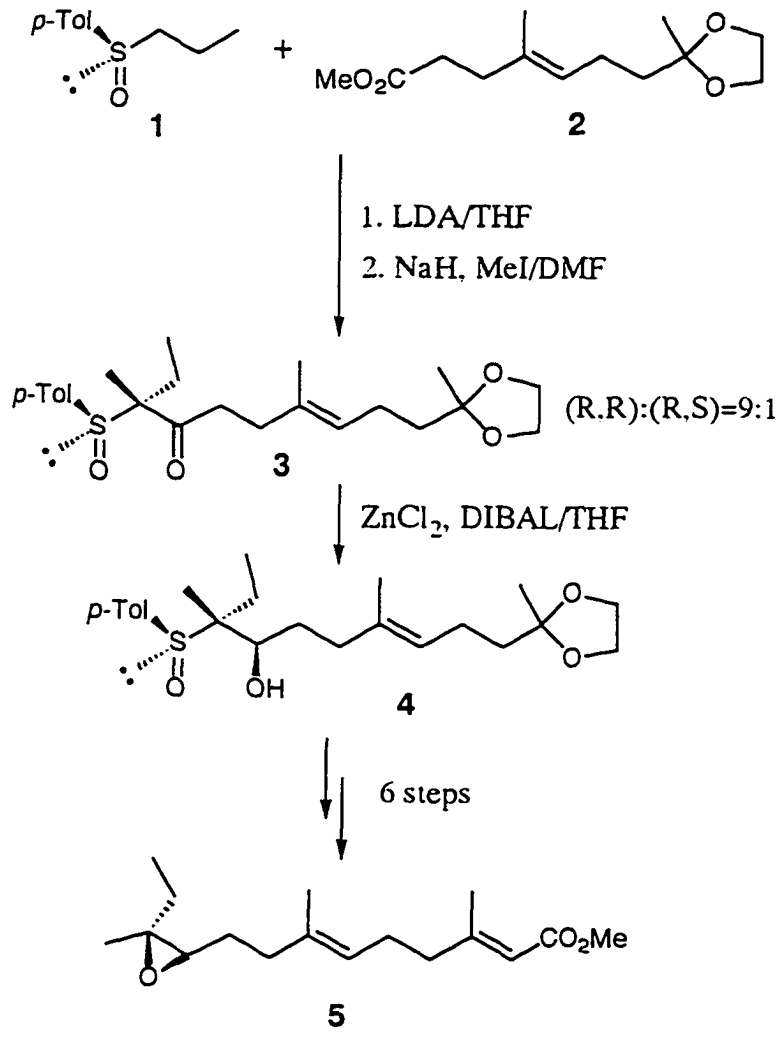

Figure 1. Application of a chiral sulfoxide in the synthesis of juvenile hormone II (**5**).

In addition to increasing our general understanding of the photochemistry and thermochemistry of sulfoxides, several other considerations make the investigations described in this thesis particularly pertinent:

1. *Future synthetic applications of the photochemical transformations of sulfoxides must be based on a mechanistic understanding of their photochemistry.* Over the past two decades, photochemical reactions of carbonyl and alkene functional groups have been used as a key step in many synthetic routes. Photochemistry has profoundly affected organic synthesis through its unique control of chem-, regio-, and stereoselectivities.[8-10] Another interest of photochemical reaction studies is the development of alternative and more environmentally benign synthetic pathways.[11] Although there are already some examples[12-15] of sulfoxide photolyses which may have potential synthetic applications, as shown in Figure 2, there are few quantitative data available concerning the effect of structure on photochemical reactivity.

2. *Use as photo-polymerization initiators.*[12,13] The radicals formed by α-cleavage, hydrogen abstraction, or β-cleavage of carbonyl compounds make them quite useful as initiators in photopolymerization.[14] By better understanding the photochemical characteristics of sulfoxides, it may be possible to explore the possibility, and eventually to develop new types of initiators. One of the potential advantages for sulfur-containing initiators is that after polymerization, their residues may still serve as antioxidants in the finished polymer products. Meanwhile, one of the disadvantages of sulfoxide initiators is their UV absorption blue shift compared to carbonyl analogs. Recent interest has been focused on the synthesis of initiators containing both carbonyl and sulfoxide functional groups.[15]

3. *Better understanding of the photodegradation of related sulfur compounds*, such as polysulfides, polysulfoxides,[16] antioxidants, and other specialty chemicals.[17] Also, in order for the synthetic application of sulfoxides (including chiral sulfoxides) to be useful, the

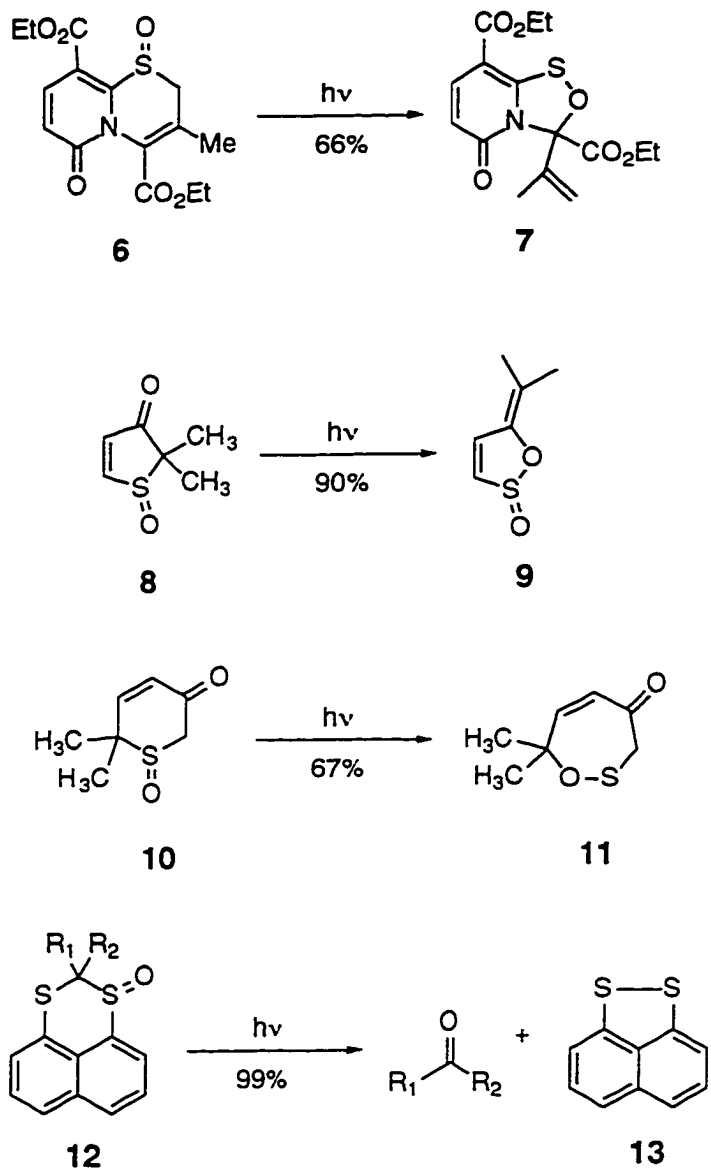

Figure 2. Examples of sulfoxide photolysis reactions with possible synthetic interest.

stability of sulfoxide intermediates (like compounds **3** and **4** in Figure 1) must be well understood. Most of those sulfoxide intermediates are alkyl aryl sulfoxides, which will be the focus in our research.

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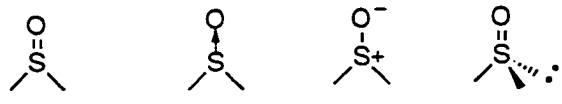
CHAPTER I

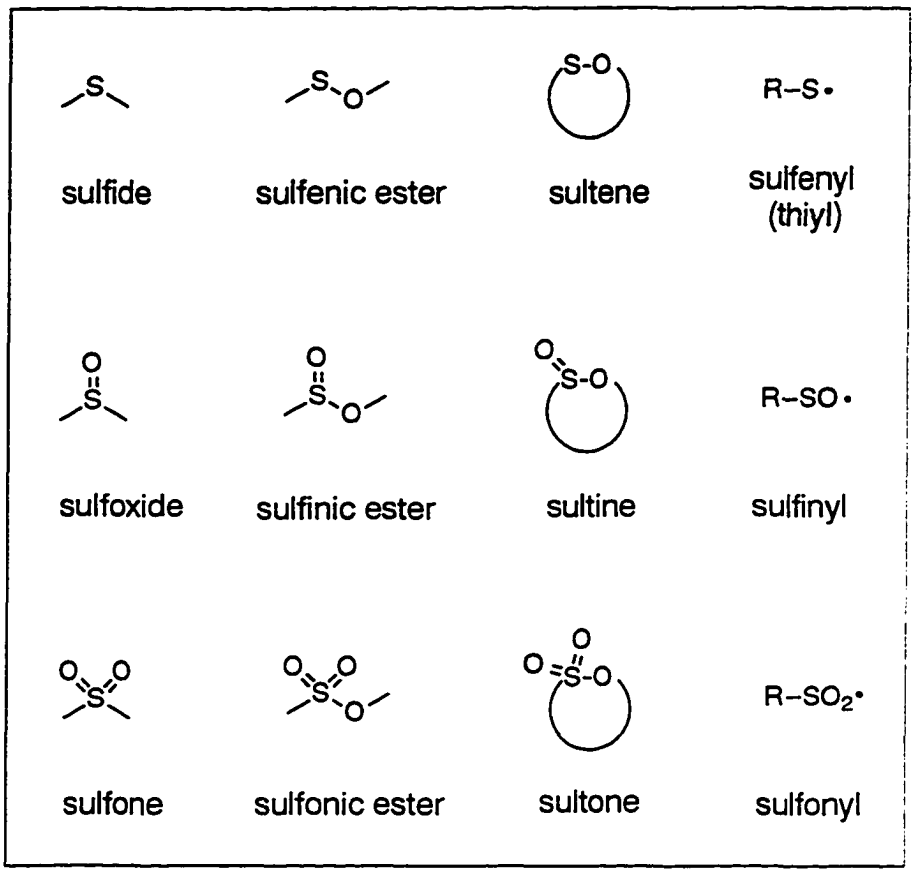
PHOTOCHEMISTRY OF SULFOXIDES: A GENERAL REVIEW

The sulfur atom in sulfoxides is generally considered to be approximately sp^3 hybridized, but the real character of the sulfoxide bond is still not very clear. The oxygen atom remains electronegative compared to the sulfur atom and is partially negatively charged. The bond strength is in the range of 85–90 kcal/mol. Perhaps because of the ambiguity regarding the sulfoxide bond, there are several ways to write its structure. The designation S=O was chosen to represent the sulfoxide bond throughout this dissertation. The electron pair is omitted except in some chiral sulfoxide cases when stereo-structure is important.



One of the features of the sulfur chemistry is the multiple oxidation states of the sulfur atom. The sulfoxide is in an intermediate state. Its simple oxidation or reduction is related to two other groups of organosulfur compounds: sulfone and sulfide. These structures along with several related compounds are listed below for reference.

Despite a fairly long history of research, the photochemistry of sulfoxides has not been fully developed or generalized.[1-5] Before our own research, it was still rather difficult to predict the outcome of the photochemical reaction of new sulfoxides, and still is, particularly when other functional groups are present. The majority of known photochemical reactions of sulfoxides can be classified into four typical classes: α-cleavage, stereomutation, hydrogen abstraction, and deoxygenation. This review will focus on the α-cleavage process, but will also cover some racemization and proposed hydrogen abstraction processes. The



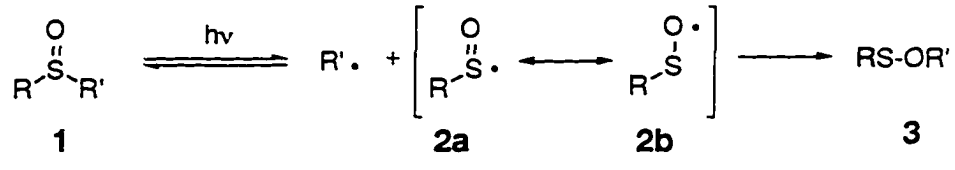
multiplicity of sulfoxide photochemistry can be seen from numerous examples throughout this chapter.

α-Cleavage

α-Cleavage of sulfoxides is the homolytic cleavage of one of the carbon-sulfur bonds. (There are examples in which both bonds cleave at the same time when high energy photolysis of small cyclic sulfoxides is carried out in the gas phase.[6]) α-Cleavage may be the most important primary reaction in the photolysis of sulfoxides. It has been proposed as the primary step for some other reactions, such as desulfurization, deoxygenation and racemization.

When a sulfoxide **1** is photolyzed, α-cleavage forms a radical pair (in acyclic sulfoxides) or biradical (in cyclic sulfoxides) in the solvent cage. The observed products

come from the expected chemistry of a radical pair or biradical. The recombination of the alkyl radical and dual-dentate sulfinyl radical (**2a** and **2b**) produces a series of cage and non-cage products. Arylsulfinyl radicals and their spin trapping products have been observed by steady state electron paramagnetic resonance (EPR) on photolysis of sulfoxides at low temperature.[7-10] Chemically induced dynamic nuclear polarization (CIDNP) was also observed in the photolysis of certain sulfoxides that appear to proceed by α-cleavage.[11,12] Recently, the properties of some arylsulfinyl radicals have been studied by both laser flash photolysis and theoretical calculations in the Jenks lab.[13]



The isolated products from photolysis of sulfoxides depend on the sulfoxide structure and reaction conditions. Up to now, the existence of sulfenic ester intermediate **3** has been generally accepted, but it has rarely been detected or isolated. Practically, the photoreactions usually do not stop at this stage. We have found that sulfenic esters are generally very photoreactive and undergo further photodecomposition, which leads to the detected products. Because of these secondary photochemical and accompanying thermal reactions, the products from photolysis of sulfoxides are very complicated. It is not unusual for different researchers to report different photolysis products from the same sulfoxide depending on the reaction conditions employed, such as solvent. irradiation wavelength, and photolysis vessel.

Acyclic sulfoxides

Dimethyl sulfoxide (DMSO)

The photochemistry of DMSO has been studied in both solution and neat. In 1963, Horner reported the production of CH_4, C_2H_6 and CO from the irradiation of neat DMSO.[14] Although no experimental detail was given, the production of CH_4 and C_2H_6 was apparently

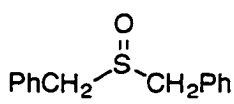
the result of α-cleavage. The carbon monoxide may be formed by over oxidation of methyl radical (CH_3•) or one of its oxidative intermediates, such as HCHO. At the same time. Schenk reported the photooxidation of DMSO by oxygen in the presence of several sensitizers.[15] Dimethyl sulfone was the only product detected, no product from α-cleavage was observed. In 1965, Sato also reported the formation of dimethyl sulfone from the UV irradiation of DMSO.[16] When the photolysis was conducted in a nitrogen atmosphere. sulfide and sulfone (both less than 1%) were detected, which was proposed to result from a photo-disproportionation reaction. However, since the recovery of DMSO is about 92%, it is possible that there may be other (gas) products from α-cleavage not detected.

In the early 1970s, Gollnick and coworkers studied the direct and sensitized photolysis of DMSO solution more thoroughly.[17] According to their results, excitation of DMSO in solution at 254 nm leads to singlet DMSO (E_S = 105 kcal/mol), which then undergoes three primary reactions: fragmentation to methyl and methanesulfinyl radicals (α-cleavage), bimolecular disproportionation to sulfone and sulfide, and deactivation to ground state. Methyl sulfinyl radicals (CH_3SO•) were proposed to undergo various reactions, including hydrogen abstraction from solvents, dimerization in neat DMSO, electron transfer to methyl radicals in water, and addition to aromatic systems, such as benzene. Methyl radicals (CH_3•) undergo hydrogen abstraction to form CH_4, whose quantum yield was used to estimate the quantum yield of α-cleavage. This may be questionable, because it ignores the recombination of the radical pairs. In dilute solution, the α-cleavage (D_{C-S} = 53 kcal/mol) is about twenty times more efficient than the disproportionation reaction. The estimated quantum yield is 0.14 which is independent of the nature of the solvent (acetonitrile, alcohols and water). Neat DMSO has an "α-cleavage" quantum yield of 0.09. Products like methane, methanesulfonic acid, dimethyl disulfide, dimethyl sulfide and methanethiosulfonate were all quantitatively analyzed. It was also found that photolysis of DMSO can be sensitized by benzene and toluene, whereas acetone and benzophenone are incapable of doing so.

Disproportionation reactions were completely suppressed by the sensitizers. In the sensitized photolysis, the major product is CH_4 (from methyl radical), while methylsulfinyl radicals ($CH_3SO\bullet$) are trapped by sensitizer or solvent. It is not clear whether these energy transfer reactions lead to the formation of a singlet excited DMSO molecule or to a singlet benzene–DMSO exciplex that subsequently decomposes to methyl and methylsulfinyl radicals.

Chen and coworkers studied the photodissociation of DMSO at 193.3 nm in the gas phase.[18] Both $CH_3\bullet$ and SO were detected as the primary products by using resonance enhanced multiphoton ionization and laser induced fluorescence (LIF) techniques, with the quantum yield of SO being nearly unity. Their result favors the hypothesis that there may exist a concerted three-center fragmentation process. Recently, the photodissociation of DMSO at 193.3 nm was also studied by using the molecular beam time of flight (TOF) mass spectrometric technique.[19] In addition to $CH_3\bullet$ and SO, $CH_3SO\bullet$ was also observed as a primary product. The analysis of the TOF data provided evidence that SO is formed via a stepwise mechanism. It was estimated that approximately 53% of the primary $CH_3SO\bullet$ radicals undergo further dissociation to produce $CH_3\bullet$ and SO.

Dibenzyl sulfoxide



4

Dibenzyl sulfoxide (**4**) is another acyclic dialkyl sulfoxide system whose ketone analog has drawn much attention due to its symmetric structure and the formation of stabilized benzyl radicals ($PhCH_2\bullet$). For compound **4**, however, it must be recognized that the phenyl groups are the primary chromophores. In 1965, Sato detected benzyl mercaptan (isolated as dibenzyl disulfide) and benzaldehyde from the photolysis of dibenzyl sulfoxide in benzene under nitrogen.[16] Later, more products were identified: benzaldehyde (37%), dibenzyl disulfide (14%), dibenzyl (1%), and benzyl alcohol (4%).[20] In a laser flash

photolysis study of some aromatic sulfur compounds,[21] Thyrion and coworkers found that dibenzyl sulfoxide exhibited one band at 317 nm, which was assigned to the benzyl radical.

Other dialkyl sulfoxides

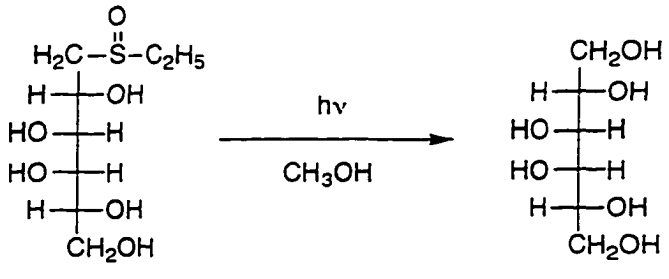
In 1966, Petrova and Freidlina reported the decomposition of di-n-butyl and di-isopropyl sulfoxides under UV light at 60 °C.[22] The identified products were *n*-butyraldehyde, *n*-butyl mercaptan, and di-*n*-butyl disulfide from photolysis of di-*n*-butyl sulfoxide. Diisopropyl sulfoxide gave acetone and diisopropyl disulfide as products. It was postulated that the reactions had a homolytic character, since these carbonyl compounds could not be formed without radical initiators at this temperature.

Shelton and Davis studied the direct and sensitized photolysis of dialkyl, *t*-butyl phenyl and diallyl sulfoxide.[23] It was found that the effective sensitizers are those containing a carbonyl group. Products, which appeared to be derived from initially formed alkyl and sulfinyl radicals, supported the cleavage of the C-S bond. Also products derived from alkoxy and sulfenyl radicals indicated possible formation of a sulfenic ester, which came from the combination of alkyl and sulfinyl radical pair. It was suggested that di-*n*-alkyl sulfoxides such as DMSO, di-*n*-propyl sulfoxide and diisobutyl sulfoxide underwent only the disproportionation reactions to give a mixture of sulfides and sulfones. They accounted for the formation of disulfide from the dimerization of either two sulfenyl radicals (PhS•) or two sulfinyl radicals (PhSO•, with loss of O_2). To explain the sulfide product, they proposed the reaction between a triplet excited sulfoxide and a ground state sulfoxide with loss of molecular oxygen.

Another interesting observation was that they found moderate amounts of *t*-butyl *t*-butanethiosulfinate (*t*-Bu)S(O)S(*t*-Bu) in the sensitized photolyses of di-*t*-butyl sulfoxide. Since thiosulfinate was produced from the dimerization of sulfenic acid (RSOH), they suggested there might exist excited ("hot") ground state sulfoxides, which underwent concerted *cis*-elimination like in the sulfoxide thermal decomposition. Sulfoxides with β-

hydrogens can undergo concerted *cis*-elimination at modest temperatures leading to the formation of sulfenic acids and alkenes (see Chapter 6 for further details). It is not clear why this was only observed in the di-*t*-butyl sulfoxide case. One explanation may be that the presence of a *t*-butyl group gives a favorable conformation for β-H abstraction. Another possible explanation is efficient hydrogen abstraction between the sulfinyl radical and the *t*-butyl radical after α-cleavage.

Horton and Jewell reported the synthesis of galactitol (**6**) by photolysis of 1-deoxy-1-ethylsulfinyl-D-galactitol (**5**) in methanol.[24] This could be explained by generating a sulfenic ester as an intermediate. Also the cleavage of the S-C_2H_5 bond should result in some other products.



5 **6**

Alkyl aryl sulfoxides

Despite their usefulness in organic synthesis, there are only a few reports on the photochemistry of acyclic alkyl aryl sulfoxides. One of the advantages of this system is the UV absorption red-shift compared to dialkyl sulfoxides.

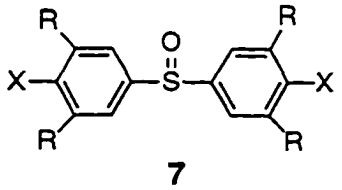
In 1981, Lüdersdorf and coworkers studied the direct and benzophenone-sensitized photochemical C-S bond cleavage of alkyl aryl sulfoxides using the CIDNP technique.[12,25] The triplet spin-correlated methyl-arylsulfinyl radical pair was indirectly detected from *ortho*-substituted aryl methyl sulfoxides. Correlation was proposed between the photocleavage reactivity and the ground state C-S bond dissociation energies of the sulfoxides.

In the past several years, the photophysics and photochemistry of a series of alkyl aryl sulfoxides have been studied in the Jenks lab.[26,27] Several proposed photochemical processes were tested (including α-cleavage, H-abstraction, stereomutation, and deoxygenation). Products were identified and quantum yields were measured. The sulfenic ester intermediates were observed and characterized. A general mechanistic scheme was proposed for this series of sulfoxides (Chapters 2-4). More recently, we were able to detect arylsulfinyl radicals by using a laser flash photolysis technique, which provides direct evidence for the primary α-cleavage process.[13]

Diaryl sulfoxides

The simplest and also most studied sulfoxide in this category is diphenyl sulfoxide. Kharasch and coworkers found biphenyl (53%), diphenyl sulfide (7%) and a small amount of diphenyl disulfide from the photolysis of diphenyl sulfoxide in benzene,[28] which supported the C-S bond cleavage pathway. The phenyl radicals from α-cleavage reacted with benzene to form the phenylcyclohexadienyl radical, and biphenyl was produced by hydrogen abstraction from this intermediate. Homolytic C-S bond cleavage was also consistent with a brief flash photolysis study of diphenyl and 4,4'-ditolyl sulfoxides.[21] The transient absorption spectra show common bands at 312 and 420 nm, which were attributed to the arylsulfinyl radicals.

In 1978 and 1980, Gilbert and coworkers studied the photolysis of diaryl sulfoxides **7** using e.s.r. spectroscopy and detected some very weak signals at low temperature, which were assigned to the aromatic sulfinyl radicals.[8,9] Corresponding radical-adducts were also detected in the presence of spin traps.

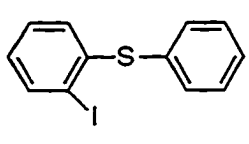


7

R = H, *t*-Bu
X = H, Me, Br, OH

A mixture of α–, β–, and γ-isomers of *p*-tolylpyridine was obtained in almost quantitative yield from the photolysis of di-*p*-tolyl sulfoxide in pyridine.[29] The ratio of product isomers was almost identical to those when *p*-tolyl radical was generated by other methods, [30] which also supported the α-cleavage radical mechanism.

In 1976, Kharasch and Langford studied the photolysis of 2-iodophenyl phenyl sulfide (**8**), sulfoxide (**9**) and sulfone (**10**) in benzene.[31] Analysis of the products derived from aryl-I cleavage and aryl-S cleavage shows an interesting trend for the efficiency of C-S bond cleavage: C-S (sulfide) > C-SO (sulfoxide) > C-SO_2 (sulfone). This result may help to achieve desired organic transformations by choosing different sulfur oxidation states.



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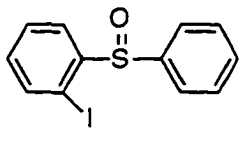

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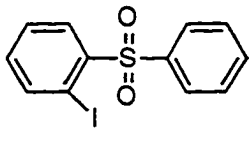


10

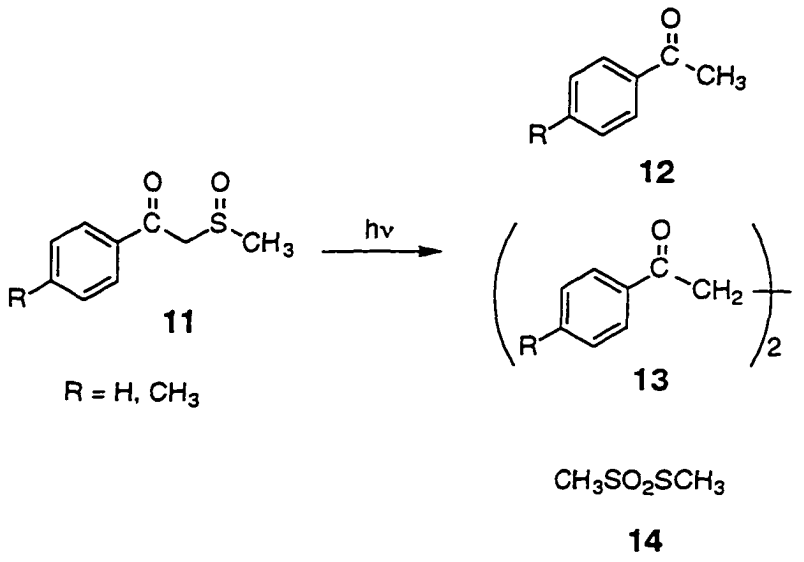
	8	**9**	**10**
$\frac{\text{C-I cleavage}}{\text{C-S cleavage}}$	$\frac{4}{3}$	$\frac{4}{1}$	$\frac{10}{1}$

Acyclic ketosulfoxides

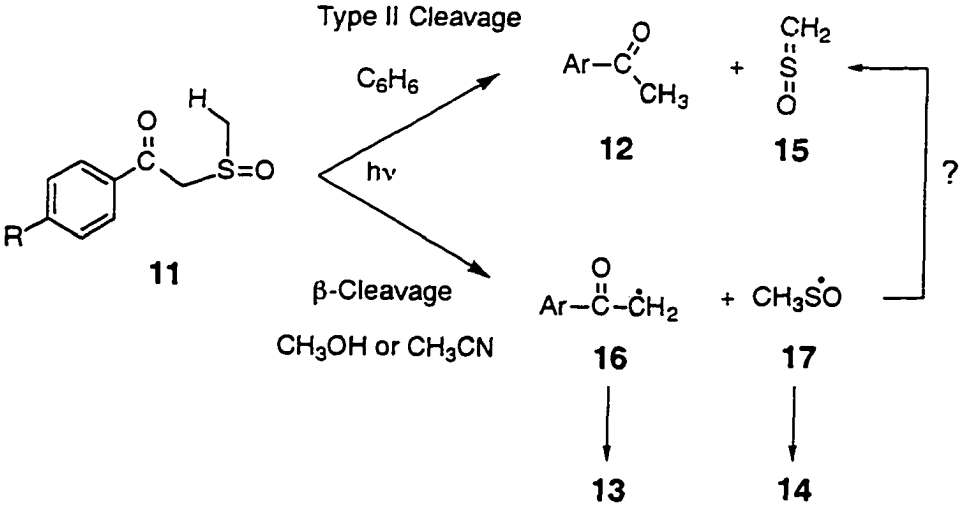
Acyclic ketosulfoxides have drawn much attention duo to their potential application as polymerization initiators and widespread synthetic application of their corresponding thermal chemistry.[35] When considering the photophysical properties of carbonyl and sulfinyl groups, it is apparent that the low energy chromophore is the ketone in this class of compounds. However, most of the bond cleavage occurs near the sulfinyl group. Thus, this is basically a β-cleavage reaction of the ketones.

In 1971, Majeti reported the photochemistry of two β-ketosulfoxides (**11**).[32] Although the products support the α-cleavage process, the results are more like ketone n-π* triplet excited state chemistry than sulfoxide singlet α-cleavage chemistry (in which case the

disulfide would be produced from the cleavage of the sulfenic ester intermediates, see subsequent chapters). There are two possible pathways to explain the products from the photolysis of **11**. It was suggested that β-ketosulfoxides undergo ketone β-cleavage (which also happens to be sulfoxide α-cleavage) in methanol or acetonitrile as evidenced by the isolation of more diaroylethanes **13**. The higher yield of acetophenone **12** in benzene suggested a ketone type–II elimination mechanism as the major pathway. It is also possible



12 **11** **13** **14**

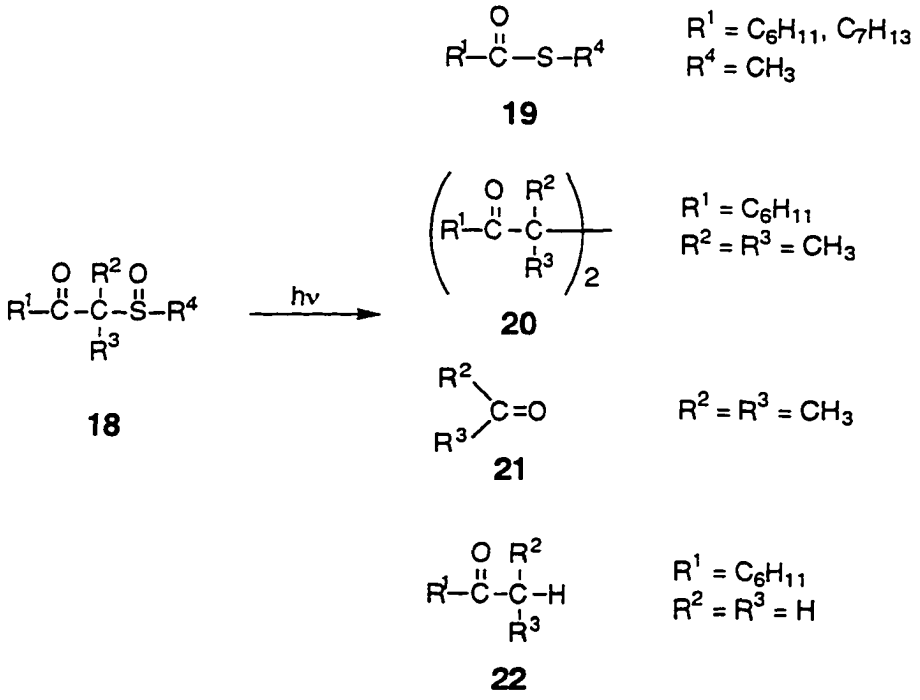


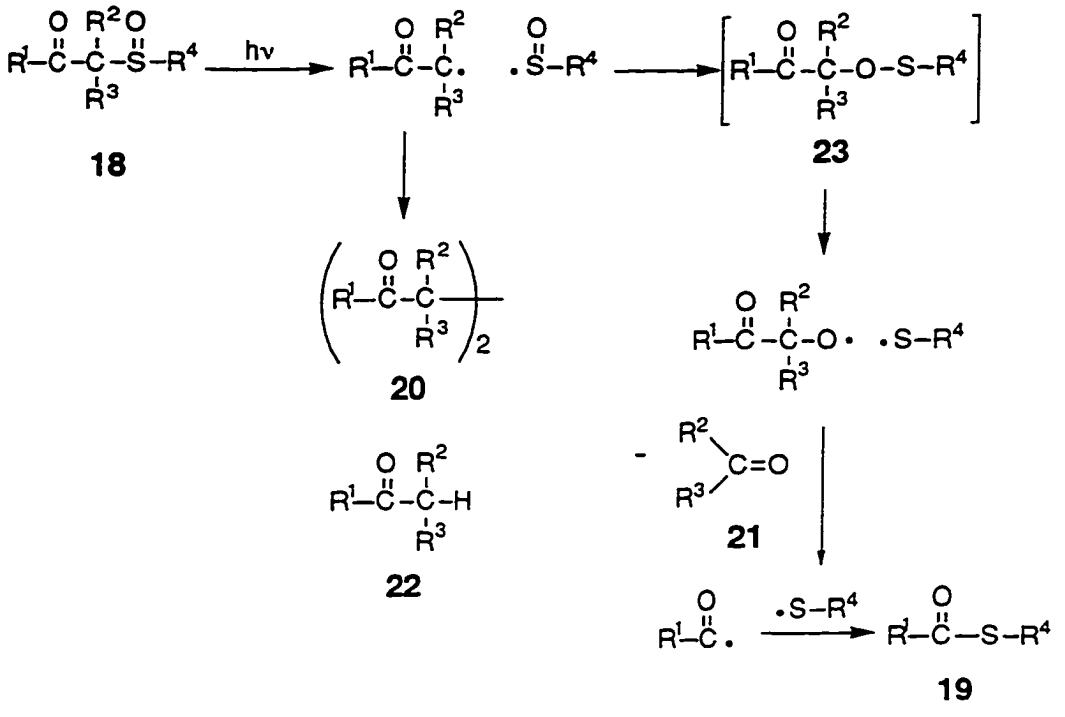
11 **12** **15** **16** **17** **13** **14**

that **12** and **13** could be produced from the disproportionation (or hydrogen abstraction) of radical pair **16** and **17**. α-Cleavage of the ketone seems unimportant in this class of compounds, which might be explained by the bond energy difference between C-C(O) and C-S(O).

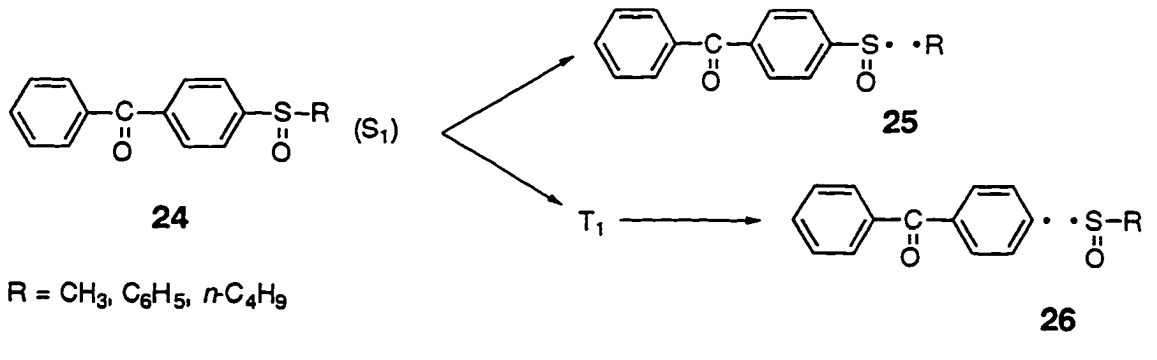
Nozaki and coworker also studied the photolysis of methyl phenacyl sulfoxides **11** (R = H) in alcohols almost at the same time.[33] They found that the product distribution was quite sensitive to the pH of the reaction media. Slightly basic conditions favored the formation of dibenzoylethanes **13**, whereas acetophenones **12** are mainly produced under acidic conditions. Aromatic substituents also affect the product distribution.

Ganter and Moser studied the photochemistry of β-ketosulfoxides **18** with different α-substituents in pentane and ether.[34] A mechanism was proposed to explain the products **19-22**, which included ketone β-cleavage and ketone α-cleavage similar to sulfoxide **11**. From our present knowledge of sulfoxide photochemistry, all the products can be rationalized by assuming the sulfenic ester **23** as the intermediate.





Recently, Fouassier and coworkers studied the ketosulfoxide derivatives **24** as photo polymerization initiators by time-resolved laser spectroscopy.[36] The proposed general diagram of the excited-state chemistry is unusual. It shows a dual path of photolysis, the singlet state cleaves at the S-R bond, and the triplet generates aryl and alkylsulfinyl radical pair **26**.



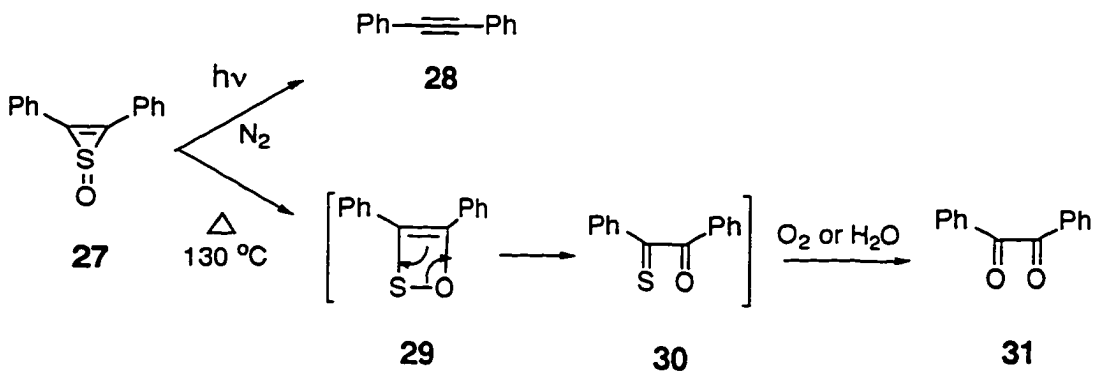
Cyclic sulfoxides

It has been known for some time that cyclic sulfoxides can undergo C-S bond cleavage under UV photolysis conditions. Most products are consistent with a possible sulfinyl-alkyl biradical intermediate, although theoretically there are other possibilities, such as heterolytic cleavage or bond-shift. The fate of the biradical depends both on the ring size and its substituents. Loss of SO and formation of ring-expanded sultenes are the two major processes. Other products are apparently formed from sultene intermediate decomposition. Some products were also rationalized by assuming hydrogen abstraction as the primary photochemical process.

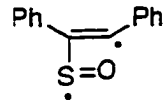
Photoextrusion of SO

SO extrusion of sulfoxides can happen either photochemically or thermally, although the sulfoxides are not as well studied and synthetically useful as SO_2 extrusion from sulfones. This reaction requires the cleavage of two S-C bonds, which may in principle proceed by either stepwise or concerted pathways. One of the driving forces is the relief of the cyclic strain, and in some cases, an aromatic system is formed.

In 1979, Carpino reported near quantitative yields of diphenylacetylene **28** from the photolysis of 2,3-diphenylthiirene 1-oxide (**27**) in benzene.[37] In comparison, thermolysis gave benzil (**31**) as the only product. Two different paths were proposed for the formation of these products.

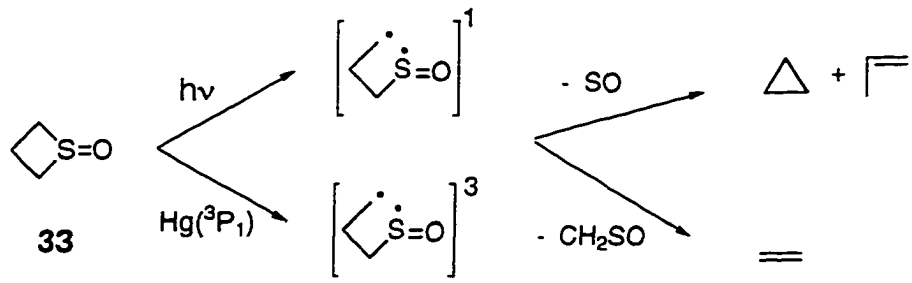


It is postulated that under photolysis conditions the cleavage of the two C-S bonds must be simultaneous or the cleavage of the second C-S bond of biradical **32** must be faster than the formation of the four-membered ring sultene **29**. Another explanation is the possible triplet spin multiplicity of the biradical intermediate **32**. Otherwise, one should expect the formation of benzil (**31**).



32

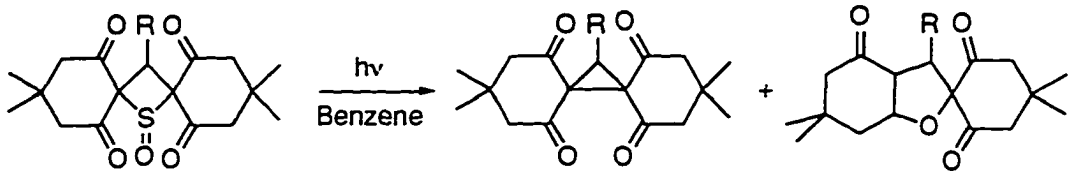
The direct or $Hg(^3P_1)$-sensitized photolyses of trimethylene sulfoxide (**33**) in the gas phase gave a mixture of ethylene, propylene, and cyclopropane.[38] Product ratios were affected by both pressure and excitation wavelength. The suggested mechanism involves initial cleavage of a C-S bond to produce a biradical intermediate **34** which could undergo intramolecular randomization of the available energy and give the observed products.



33 **34**

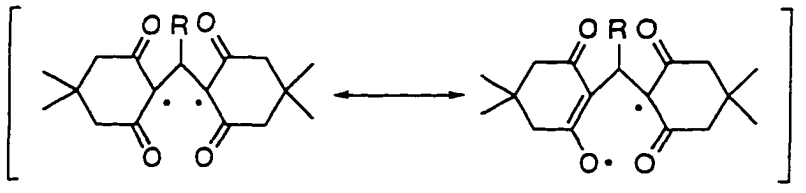
Recently, Weiner and coworkers studied the gas phase photodissociation of some cyclic sulfoxides, $(CH_2)_nSO$ (n = 2,3,4) at 193 and 248 nm.[39] The tetramethylene sulfoxide has been shown to eliminate SO via a sequential bond cleavage process, while the trimethylene sulfoxide and ethylene episulfoxide appear to undergo concerted bond cleavage to produce sulfur monoxide. In all three cases, the observed photochemistry at 193 nm appears to be occurring from the singlet electronic surface, while the 248 nm photolysis may occur from the triplet surface.

The photochemical SO extrusion of 2,2,4,4-tetraacylthietane 1-oxides (**35**) was reported by Ito and coworkers in 1978 to give a mixture of **36** and **37**. The actual chromophore in **35** should also be the ketone.[40] This is very similar to the acyclic β-ketosulfoxides described on page 15. The intermediates are apparently the biradicals **38a** and **38b**, which are formed from α-cleavage of the two C-S bonds and loss of sulfur monoxide.



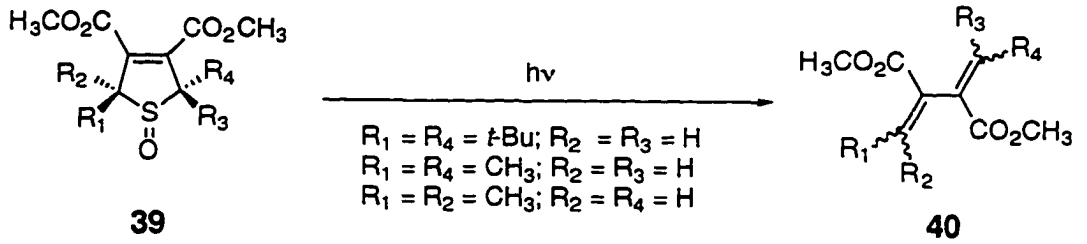
35 **36** **37**

R = H, CH_3, $CH(CH_3)_2$



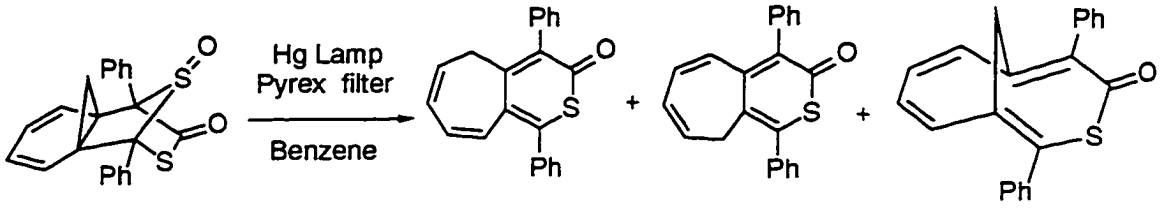
38a **38b**

In 1974, Kellogg reported the photolysis of 2,5-dihydrothiophene S-sulfoxides **39**.[41] Usually the products are mixture of diene isomers **40**.



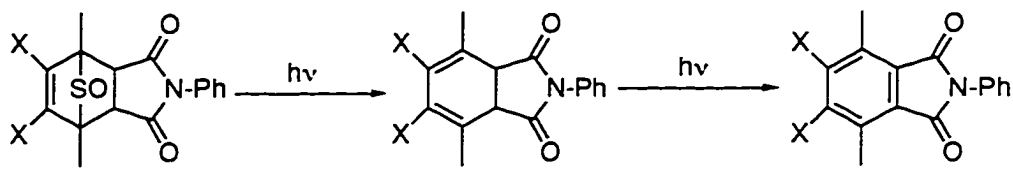
39 **40**

In 1983, Kato and coworkers studied the photolysis reaction of **41**. Products **42-44** were produced from the extrusion of sulfur monoxide and cleavage of the cyclopropane ring.[42]

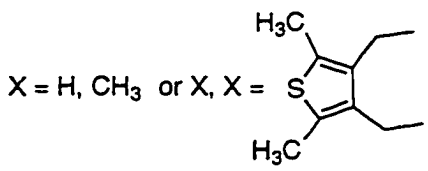


41 **42** **43** **44**

Recently, Thiemann[43] studied both direct and benzophenone-sensitized photolyses of 7-thiabicyclo[2.2.1]hept-2-ene 7-oxides **45**. The extrusion of the SO-bridge occurred concurrently with oxidation. A diene **46** was proposed as the intermediate.

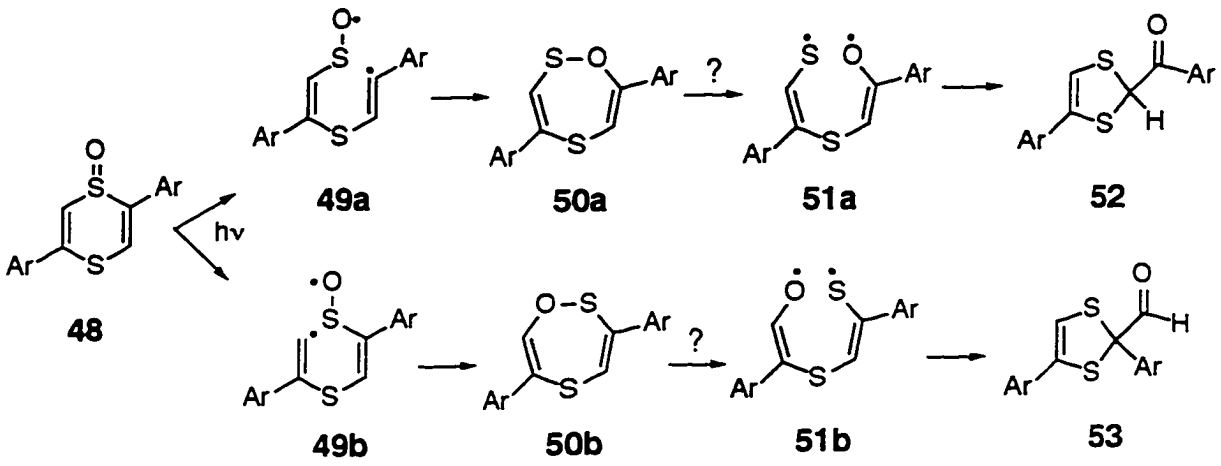


45 **46** **47**

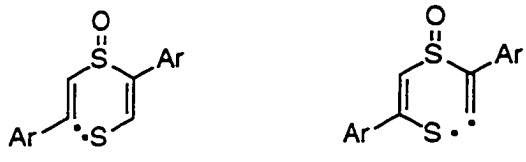


Dithiin-monoxide system

Kobayashi and coworkers reported the photolysis of 2,5-diphenyl-1,4-dithiin-1-oxide **48** in methanol and proposed the following mechanism based on the isolated products **52** and **53**.[44,45] One of the seven-member heterocyclic intermediates **50a** (Ar = C_6H_5) was isolated later by Gajurel[46] in 4% yield from the photolysis of 2,5-diphenyl-1,4-dithiin-1-oxide (**48**, Ar = C_6H_5) at 254 nm in DMSO.

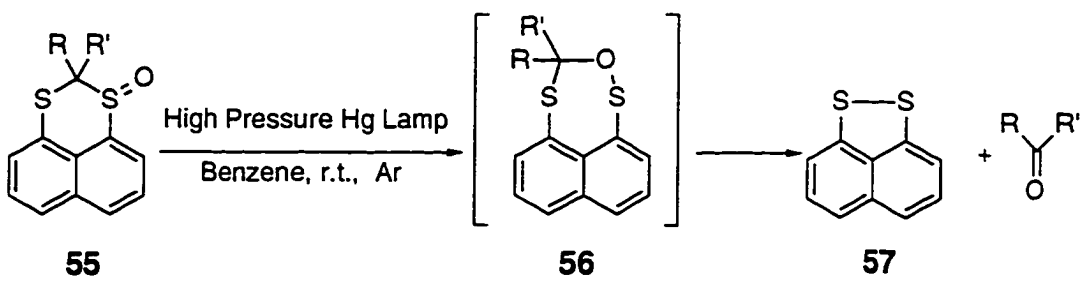


Ar = C_6H_5, *p*-ClC_6H_5, *p*-$CH_3C_6H_5$



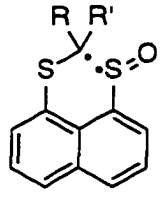
Sulfide α-cleavage from compound **48** is not observed even though the sulfide S-C bond strength is usually comparable to that of the sulfoxide S-C bond. One reason for the observation of selective sulfoxide α-cleavage may be that the recombination of vinyl-sulfenyl biradical **54a/54b** forms only the starting compound. It is still not clear whether the decomposition of **50a** and **50b** is a thermal process or a photochemical process.

In 1994, Furukawa[47] reported the photolysis of naphthol[1,8-de]dithiin monoxides **55**. Aldehydes or ketones were obtained in almost quantitative yield.



R = alkyl, aryl; R' = H, alkyl, aryl

They proposed that the sultene-like intermediate **56** may be formed from the intramolecular migration of the sulfinyl oxygen atom to the 2-carbon atom via a special S-S spatial interaction. However, another possibility for the formation of **56** involves a biradical intermediate **58** formed from α-cleavage of the starting sulfoxide. Here there may also exist a competition between sulfoxide α-cleavage and sulfide α -cleavage. It seems only the former is the productive process.

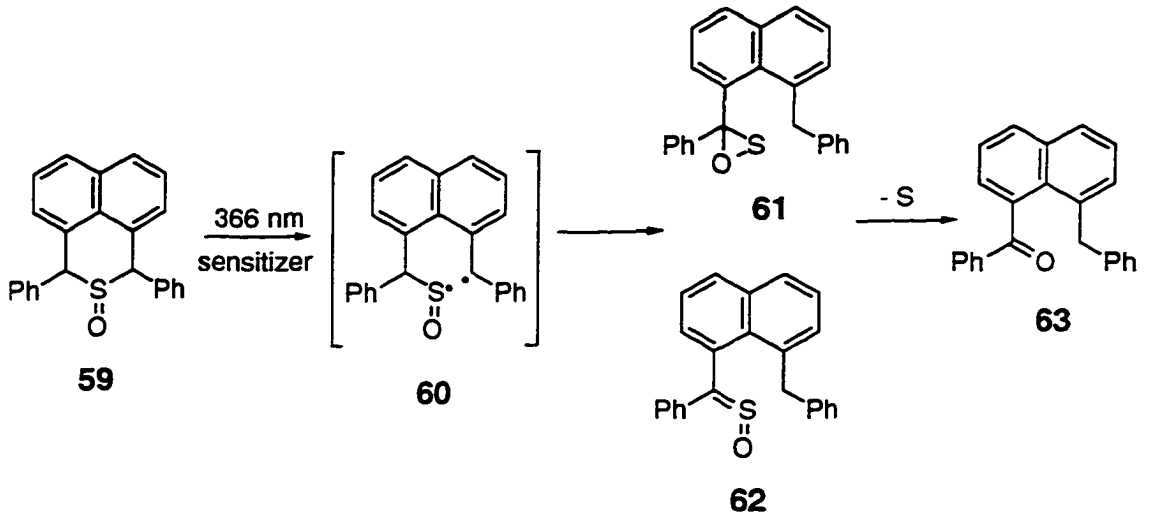


58

Other cyclic sulfoxide systems

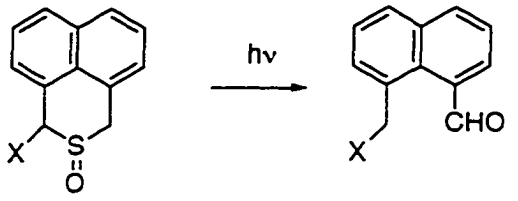
Most of the cyclic sulfoxides in this category are six-membered ring systems. Small structure changes within these systems may change the mechanism and the final products. Two mechanisms can be proposed. Each mechanism includes the combination of an α-cleavage step and a hydrogen abstraction step. The difference is the order of the two steps. Because most of these mechanisms were derived only from the analysis of the isolated products, it is difficult to distinguish between them without characterization of the intermediates and/or kinetic studies. Also, because not all the photolysis products are isolated and/or characterized, the mechanism derived from the detected products may not reflect all the processes.

In 1968, Schultz reported the benzophenone-sensitized photolysis of *cis* and *trans*-1,3-dihydro-1,3-diphenyl-2-thiaphenalene 2-oxides (**59**).[48] The only product was 1-benzoyl-8-benzylnaphthalene (**63**) obtained in 80% yield. It was proposed that sulfoxide **59** underwent α-cleavage to give a biradical **60**. The final product may come from desulfurization of a sulfine **62** or a three-membered ring heterocyclic intermediate **61**.

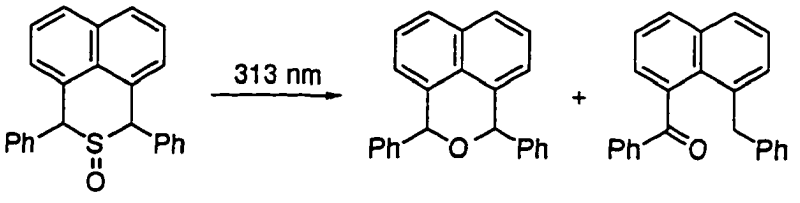


Some monosubstituted sulfoxides **64** can also be converted to aldehydes **65** in high yield under sensitized photolysis conditions.[49] α-Cleavage occurs on the carbon with substitution, probably because that radical intermediate is more stable.

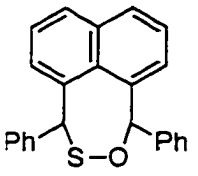
In 1973, Schultz reported the direct photolysis of *cis*- and *trans*-1,3-dihydro-1,3-diphenyl-2-thiaphenalene 2-oxides **59** and the formation of **63** and **66**.[50] It was proposed that the chemistry arised from the singlet state of the starting sulfoxides due to the difference in product formation from the triplet-sensitized experiment.



X = Et, OMe, Ph

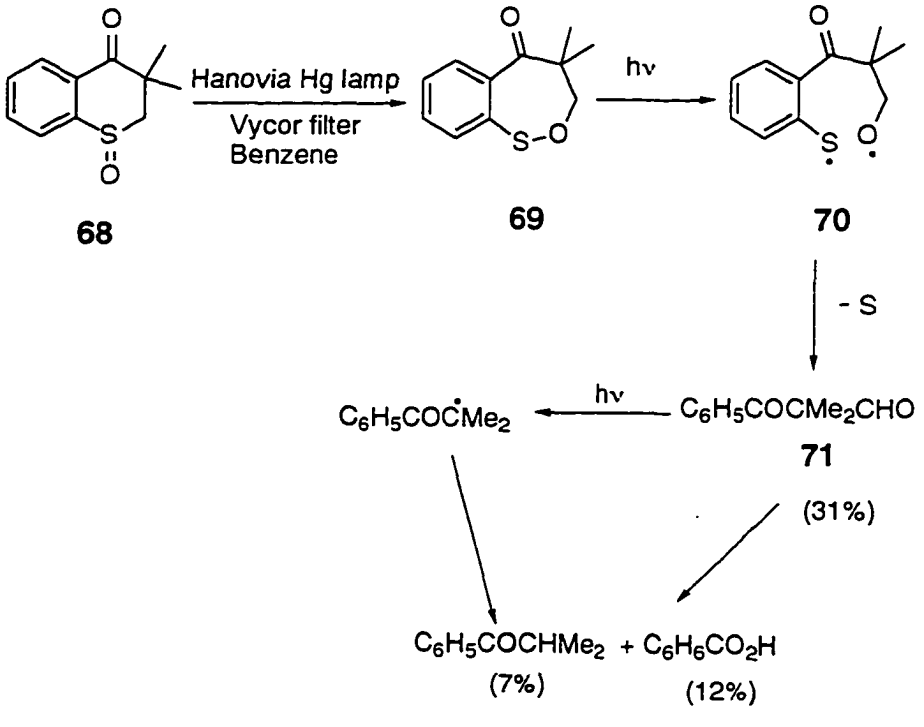


The intermediate for the formation of compound **66** was suggested to be the sultene **67**, which was isolated as an unstable oil. But the mechanism for this transformation is still not clear. Attempted purification of this intermediate only resulted in decomposition.

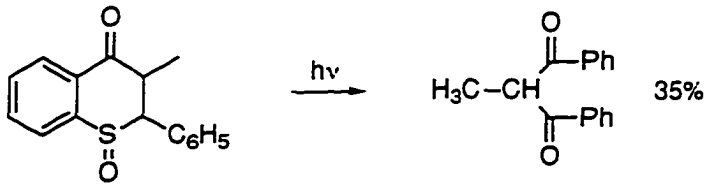


67

In the 1970's, Still and coworkers studied the photochemistry of a series of thiochromanone sulfoxides, which turned out to be remarkably sensitive to substitutions. Adding further complication to the interpretation is the presence of the lower energy carbonyl chromophore. An α-cleavage mechanism was proposed to rationalize the products from the photolysis of sulfoxide **68**.[51] A similar mechanism might apply to the photolysis of 3-methyl-2-phenylthiochroman-4-one 1-oxide **72**.

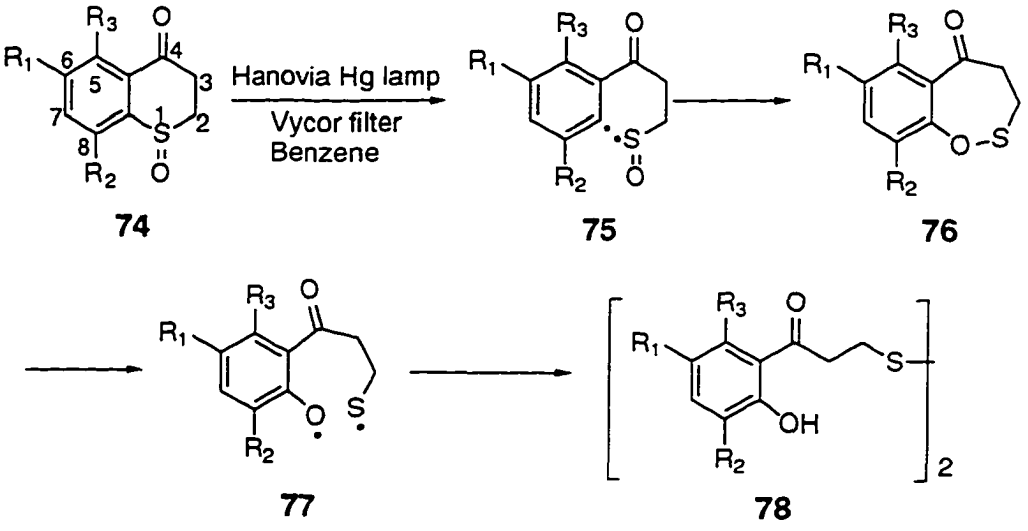


68 **69** **70** **71**



72 **73**

Although Still and coworkers found that 5-methylthiochroman-4-one 1-oxide (**74**) (R_1 = R_2 = H, R_3 = CH_3) was relatively inert to photolysis, disulfides **78** (R_2 = R_3 = H, R_1 = CH_3; R_1 = R_3 = H, R_2 = CH_3) were produced from the photolysis of its 6-methyl and 8-methyl sulfoxide isomers **74**, which suggested the possible existence of sultene intermediate **76**. A similar disulfide was also isolated from the photolysis of 6-methoxythiochroman-4-one 1-oxide **74** (R_1 = OCH_3, R_2 = R_3 = H). No disulfide was found from its 8-methoxy isomer **74** (R_1 = R_3 = H, R_2 = OCH_3). The electronic influence of the substituents on the benzene ring seems to have a distinct effect on the mechanism.



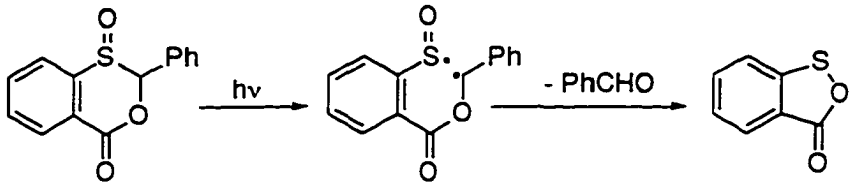
74 **75** **76**

77 **78**

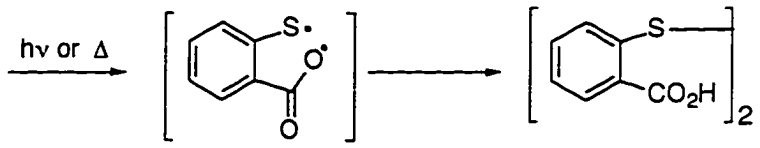
R_1 = H, R_2 = CH_3, R_3 = H	10%
R_1 = CH_3, R_2 = H, R_3 = H	4%
R_1 = OCH_3, R_2 = H, R_3 = H	5%

Noticeable in the above reaction is the surprising homolytic cleavage of the S-aryl bond. Since the yield of product **78** is very low, there may be other undetected products from S-alkyl cleavage (breaking S1-C2 bond).

A related reaction was reported by Larsen and coworkers on the photochemistry of 3-substituted 4-thioisochroman-1-one-4-oxide (**79**).[52] An α -cleavage mechanism was proposed to explain the disulfide **83** and benzaldehyde products. Though intermediate **81** was not detected, the corresponding Se and Te compounds are known to exist.

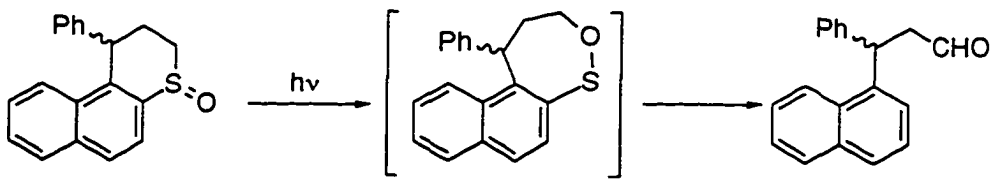


79 **80** **81**



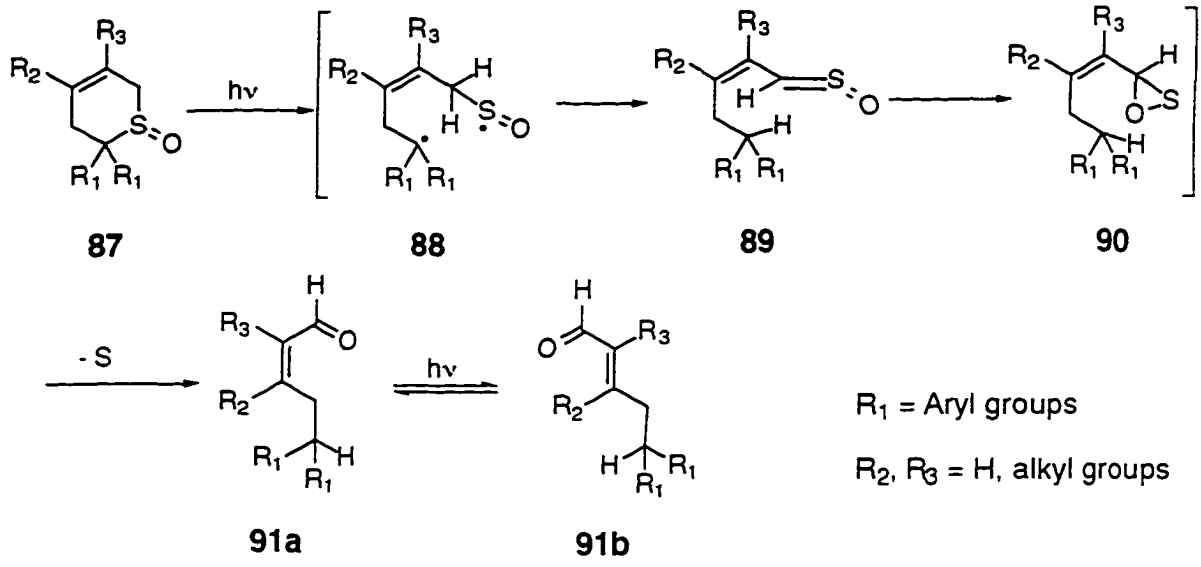
82 **83**

In the naphtho[1,2-*b*]thiopyran and naphtho[2,1-*b*]thiopyran sulfoxide systems,[53] the corresponding sulfides were produced in most cases. This deoxygenation process is obviously not standard α-cleavage chemistry. In one exceptional case, a trace of aldehyde **86** was also isolated from photolysis of **84**, which might suggest a possible pathway involving α-cleavage and sultene intermediate **85**.



84 **85** **86**

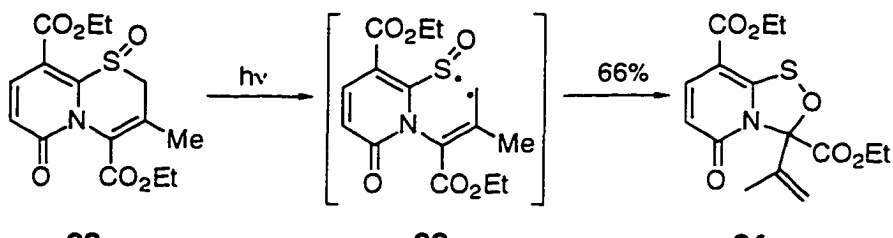
In 1980, Praefcke and coworkers found that UV irradiation of dihydro-2H-thiopyran S-oxides **87** in benzene led to the E/Z isomers of α, β-unsaturated aldehydes **91a-b**.[12,54] An α-cleavage mechanism involving sulfine intermediate **89** was proposed.



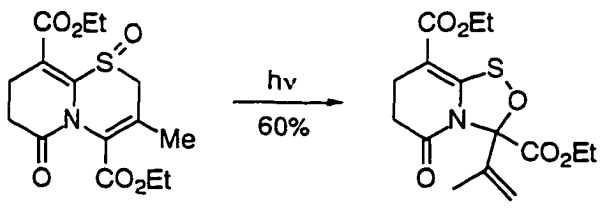
87 **88** **89** **90**

91a **91b**

From the photolysis of fused 1,3-thiazine S-oxides **92** and **95** in dioxane.[55] 2,1,4-oxathiazolidines **94** and **96** could be obtained in high yields. These appear to arise by an α-cleavage mechanism, and their structures were supported by X-ray single crystal analysis. The unique transformation and good yields may imply possible synthetic application.

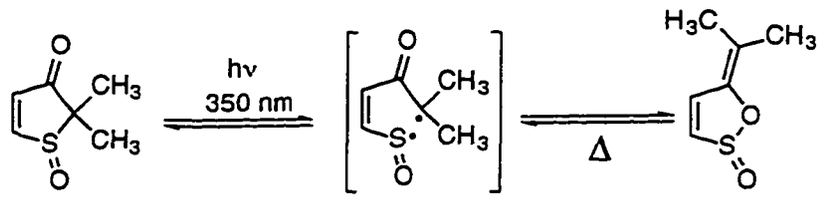


92 **93** **94**



95 **96**

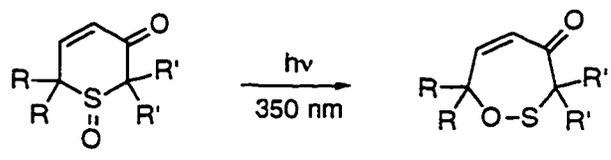
Kowalewski and coworkers found that 5-isopropylidene-1,2-oxathiole 2-oxide (**99**) could be obtained in high yield (90%) from the photoisomerization of 2,2-dimethyl-3(2H)-thiophenone 1-oxide (**97**).[56] They also observed that **99** could re-isomerize back to starting compound **97** at a higher temperature.



97 **98** **99**

It is interesting to compare this cyclic ketosulfoxide photoreaction with those of acyclic ketosulfoxides described earlier. The homolytic α-cleavage of S–C bond (β position relative to carbonyl group) is the major process in both cases. Fewer products were produced in the cyclic ketosulfoxide photolyses (biradical intermediates) compared to the acyclic cases (radical pair intermediates).

In 1993, Kowalewski reported the photoisomerization of 2H, 6H-thiin-3-one 1-oxides **100** to 3H, 7H-[1,2]oxathiepin-4-ones **101**.[57] Although it appears to be α-cleavage of the sulfoxide, the actual chromophore is probably the α,β-unsaturated ketone as in **97**. The stability of the seven-membered ring sultenes depends mainly on its substitutions. When R = R' = CH_3, the sultene was isolated in 48% yield using low temperature chromatography. When R = CH_3, R' = H or R = H, R' = CH_3, the sultenes were too unstable to be isolated, only the sultene decomposition products were isolated.

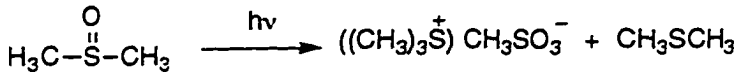


100 **101**

α-Cleavage of sulfoxides promoted by other chemical species

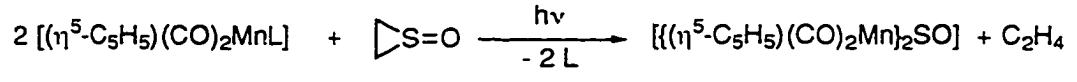
The transformations in this category are not strictly sulfoxide photochemistry. They are included because the overall reaction is related to the S-C bond cleavage, and some of them may have synthetic interest.

An early observation by Kharasch and Lowe[1] showed that extended irradiation of a solution of iodine in DMSO affords trimethylsulfonium methanesulfonate (**102**) and dimethyl sulfide. A trace of **102** was also formed in the absence of iodine. Although there is C-S bond cleavage in this reaction, the mechanism is still not clear.



102

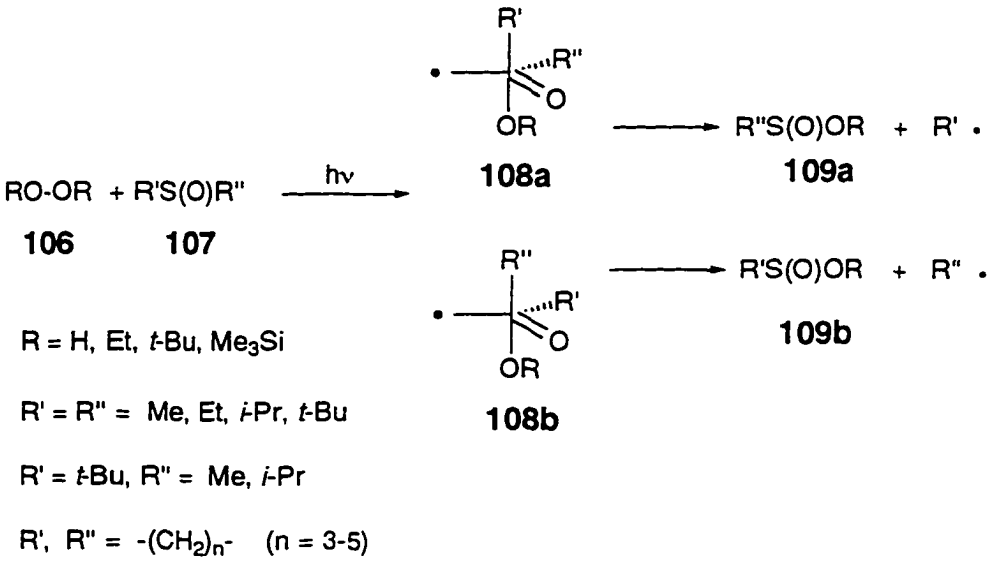
As mentioned earlier, photolysis of cyclic sulfoxides can give extrusion of sulfur monoxide - a reaction analogous to the extrusion of carbon monoxide from ketones. Unlike carbon monoxide, sulfur monoxide is extremely unstable in the free state, many attempts to isolate this species have failed. In 1985, Lorenz reported the photolysis of thiirane S-oxide **104** with extrusion of SO which was trapped by a carbonylcyclopentadienylmanganese complex **103**.[58] The sulfur monoxide complex **105** was isolated in 30% yield.



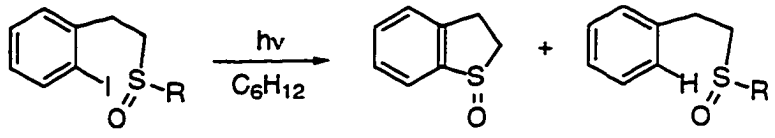
103 **104** **105**

In 1977, Gara and coworkers[59] studied the dealkylation reactions of dialkyl sulfoxides **107** in the presence of alkoxyl and trimethylsiloxyl radicals at 233 K using electron spin resonance. They found that HO• and Me_3SiO• underwent homolytic substitution (S_H2) reactions with dimethyl sulfoxide much faster than *t*-BuO•. The rate of dealkylation of symmetrical and of mixed dialkyl sulfoxides by *t*-butoxy radical increases

with the stability of the displaced alkyl radical, providing steric effects are not dominant. Siloxydealkylation of sulfoxides is faster and less selective than *t*-butoxy dealkylation, which suggested that the electrophilicity of the attacking radical was an important factor in determining rate and selectivity. The rate constant for *t*-butoxy dealkylation increases along the series $Me_2SO<Et_2SO<2\text{-}Pr_2SO$, in line with the decreasing strength of C-S bond. Although $t\text{-}Bu_2SO$ is about 11 times less reactive than $2\text{-}Pr_2SO$ because of the steric effect, *t*-Bu(Me)SO undergoes dealkylation 50 times faster than $2\text{-}Pr_2SO$. The cyclic sulfoxide underwent faster ring opening as the size of the ring decreases, which was attributed to relief of ring strain. The adduct radicals **108a-b** might exist as short-lived intermediates, although their e.s.r spectra were not detected.



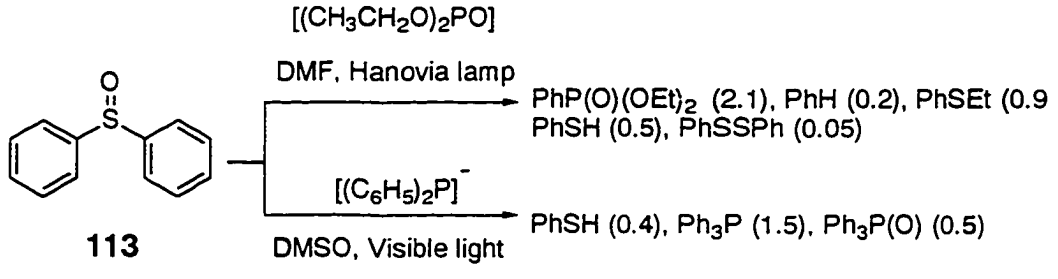
The free radical displacement reaction of alkyl 2-(*o*-iodophenyl)ethyl sulfoxide **110** in cyclohexane was studied by Kampmeier and coworkers.[60] The ratio of reduction product **112** and displacement product **111** was related to the stability of the alkyl radical (R•) and the rate of the S-C(R) bond cleavage. It was proposed that the free radical displacements at the sulfoxide sulfur involve a linear, three-center, three-electron "inversion" path. An interesting point is to see if the chirality of the sulfoxide can be preserved during this reaction.



110 **111** **112**

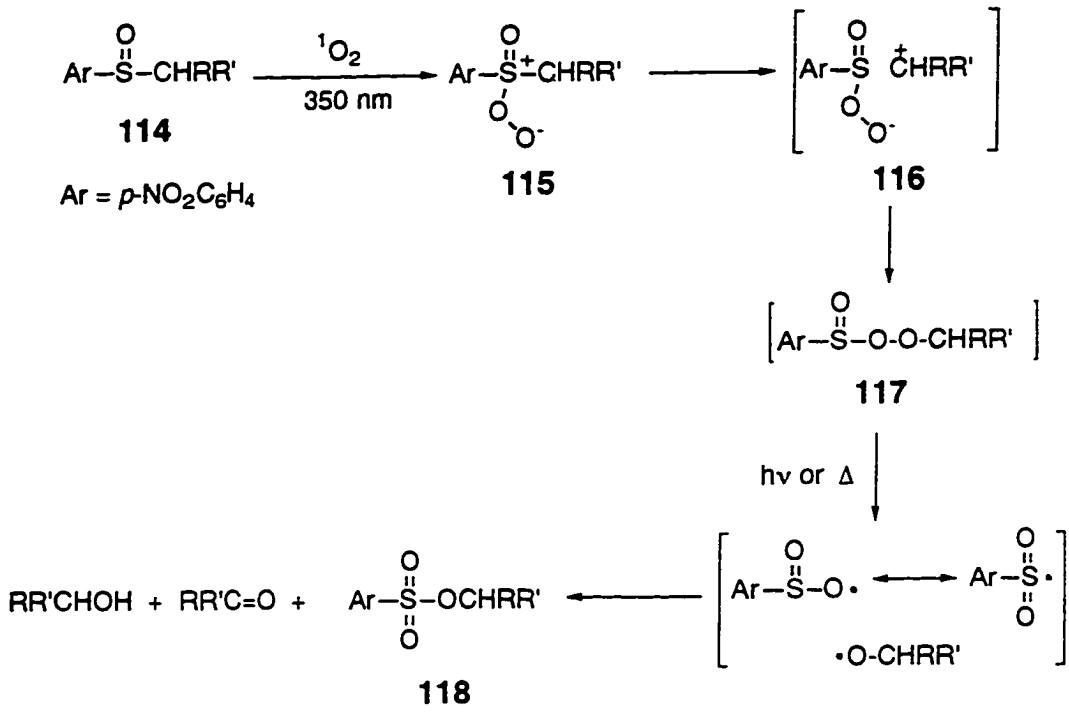
R = $-CH_3$	53	:	47
$-C(CH_3)_3$	84	:	16

A photochemical anion-promoted carbon-sulfur cleavage reaction of diphenyl sulfoxide (**113**) was reported by Cheng and Stock.[61] It was suggested that the reaction proceeds via a $S_{RN}1$ pathway and the photochemically induced electron transfer occurs in an arene-anion complex. It is possible that **113** might be reduced to diphenyl sulfide first before α-cleavage, due to the fact that all the sulfur-containing products seem to be derived from benzenethiolate (PhS^-) instead of benzenesulfenate ($PhSO^-$). The trace of diphenyl disulfide may come from the oxidation of thiophenol during workup, which was also frequently observed in other research.[27] Recently, the photolyses of sulfoxides like **113** and methyl phenyl sulfoxides in the presence of various bases has been studied, which affords deoxygenation as the major process.[62]

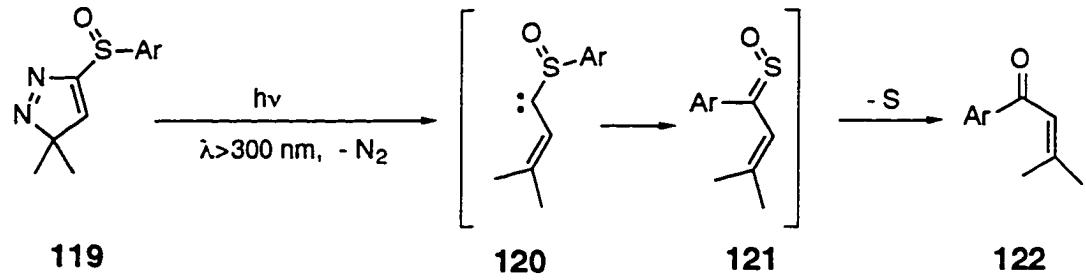


113

In a study of the photooxidation of alkyl 4-nitrophenyl sulfoxides **114**,[63] Pasto and coworkers found that the sulfoxides undergo a self-photoinduced, singlet oxygen oxidation to produce a variety of products, including sulfonates and carbonyl compounds formed by oxidative heterolytic cleavage of the C-S bond.

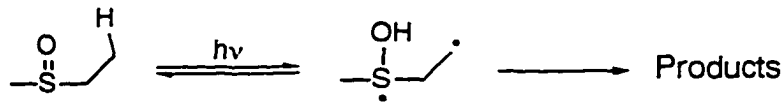


In 1979, Franck-Neumann reported the photolysis of sulfinyl pyrazoleniene **119**.[64] Vinylsulfinylcarbene **120** was proposed to be generated after irradiation, which underwent rearrangement with α-cleavage to form a sulfine intermediate **121**. Subsequent loss of sulfur formed the final product.



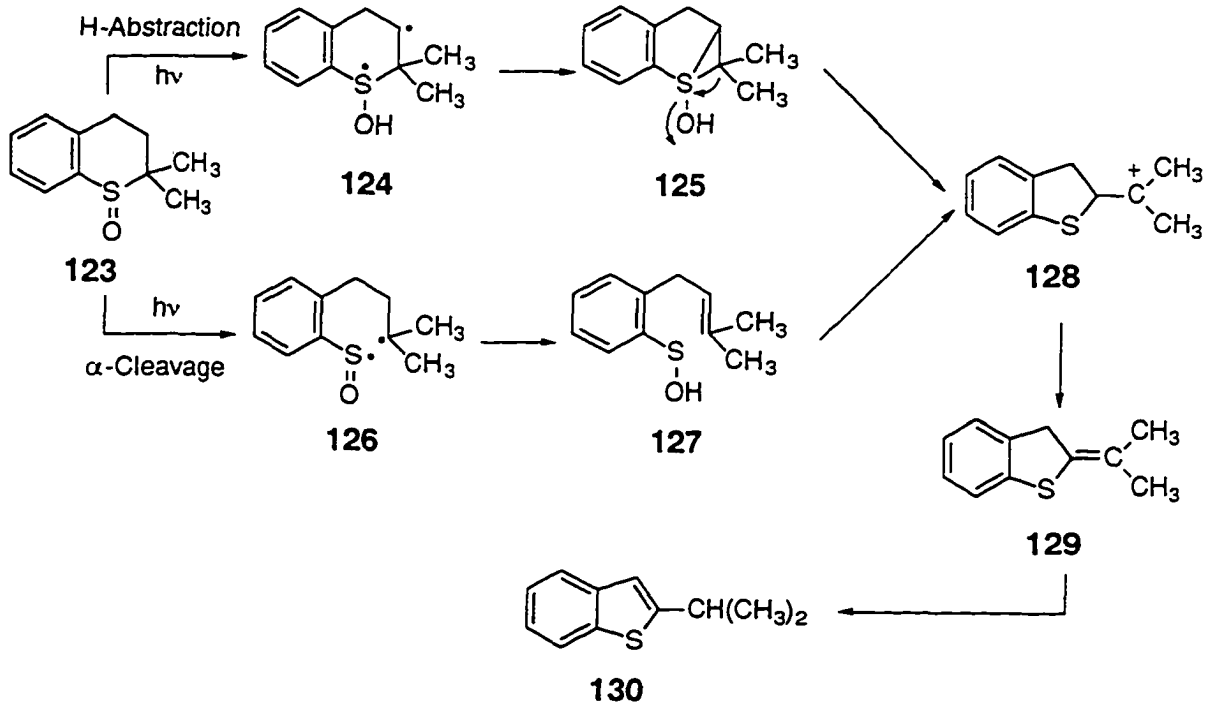
Hydrogen Abstraction

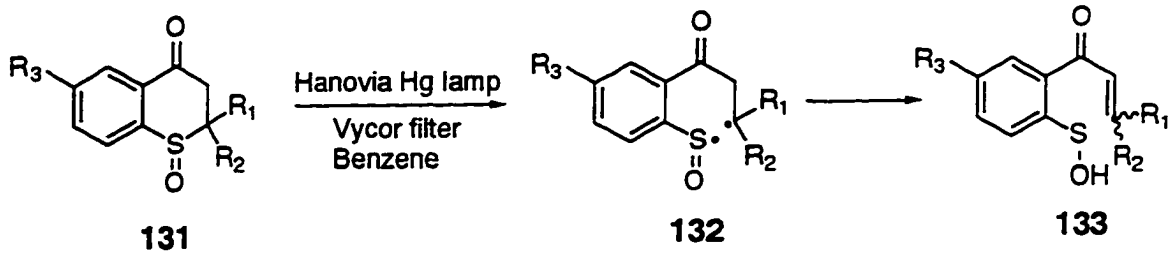
Compared to the Type II photoelimination of carbonyl compounds, the intramolecular hydrogen abstraction of a sulfoxide in the excited state is not well established. However, this mechanism has been used to rationalize some products in several sulfoxide photochemical investigations.



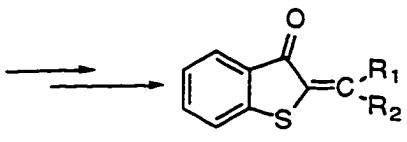
Most of the sulfoxide hydrogen abstraction examples reported before occurred in cyclic sulfoxide systems with a hydrogen at the β-position being abstracted.[50,66] The proposed transition state is a five-membered ring, rather than a six-membered ring, system proposed for carbonyl compounds.[67] Usually, these reactions can also be explained by an α-cleavage step, followed by disproportionation, and subsequent thermal chemistry of the resulting sulfenic acid.[4,50,51]

In 1966, Archer and Kitchell reported the photolysis of 2,2-dimethylthiachroman 1-oxide (**123**) in benzene.[68] The major product is 2-isopropylbenzothiophene (**130**). They proposed a mechanism which included β-hydrogen abstraction and subsequent deoxygenation steps. We suggest that the production of compound **130** can also be rationalized by an α-cleavage pathway through the common intermediate **129**.





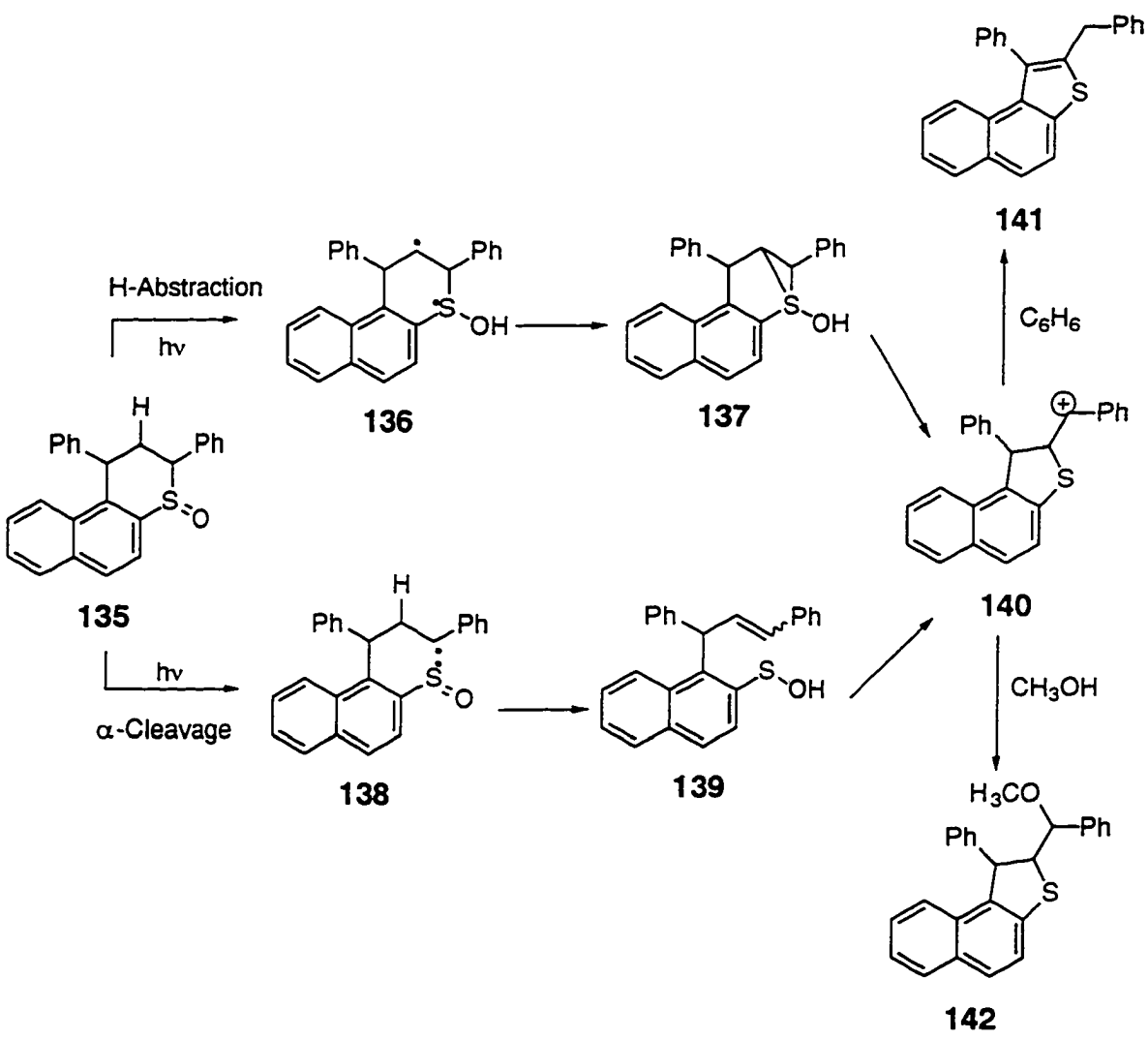
131 132 133



134

$R_1 = C_6H_5$, $R_2 = H$, $R_3 = CH_3$ (3%)

$R_1 = R_2 = CH_3$, $R_3 = H$ (13%)

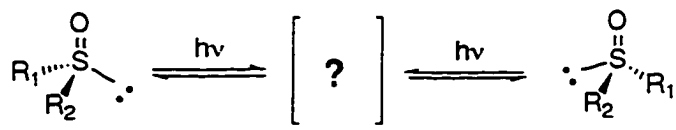


135 136 137 138 139 140 141 142

In the photochemistry of thiochromanone sulfoxides, the production of **134** from **131** can be rationalized from either α-cleavage or a hydrogen abstraction mechanism. A similar reaction, which converted **135** to **141** and **142**, was reported by Schultz and coworkers.[50] Labeling experiments showed that only the hydrogen that was proposed to be abstracted was lost. Again, an α-cleavage based mechanism can also be used to explain the experimental results.

Stereomutation

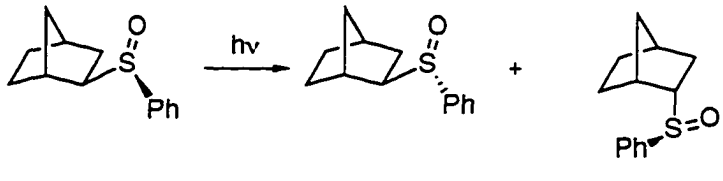
The chiral sulfoxide is a very important group of chiral auxiliaries used widely in organic synthesis.[69] One reason is the relative ease of preparing one enantiomer of a chiral sulfoxide. This functional group is usually introduced at the early stage of the multi-step synthesis and remains in the intermediates for several steps. Their chemical and configurational stabilities are critical for their successful application to asymmetric organic synthesis.



The thermal stereomutations of sulfoxides has been studied and their mechanisms are dependent on the structure of the sulfoxides.[70-74] On the other hand, there are only a few reports of the photoracemization of sulfoxides. The first synthesis of penicillin (*R*)-sulfoxides was achieved by photochemical inversion of the (*S*)-isomer.[75] The early work on the photolysis of sulfoxides by Hammond and Mislow suggests that there are substantial structural effects on their racemization.[76,77] Direct irradiation of (*S*)-naphthyl tolyl sulfoxide gave racemized starting material in 70% yield. It was found that the racemization of sulfoxides could be achieved under both intramolecular and intermolecular photosensitization

conditions.[34,76-78] In general, direct irradiation caused more decomposition than the sensitized cases. Compared to aryl alkyl sulfoxides and diaryl sulfoxides, dialkyl sulfoxides decompose without obvious racemization under either direct photolysis or photosensitization condition. This suggests that the arenesulfinyl chromophore might be required for the photoracemization. In the naphthalene photosensitization case, it was proposed that the active intermediate was an exciplex.[79] Both singlet and triplet states of naphthalene are lower in energy than the respective states of the sulfoxides. Recently, the singlet quenching of various sensitizers by a series of sulfoxides have been studied.[80] The results suggested that the mechanism for quenching involves electron transfer and/or exciplex formation. Charge (electron) transfer is from the sensitizer to the sulfoxides.

One of the examples of sulfoxide stereomutation involved a second stereogenic center.[81] From the photolysis of phenyl norbornyl sulfoxide, small amount of **145** was also detected beside compound **144**, which suggests the possible existence of an α-cleavage intermediate.



143 **144** **145**

Conclusion

From the above brief review of sulfoxide photochemistry, we can see a broad spectra of interesting reactions, although some fundamental questions are still unclear. α-Cleavage is the most cited process to rationalize sulfoxide photoreactions, but the intermediates have not been well characterized and most examples include complicating carbonyl chromophores. The efficiency of a hydrogen abstraction process remains an open question. There is still a lot of work that needs to be done before we can confidently predict the photochemical outcome of a new sulfoxide.

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CHAPTER II

PHOTOCHEMISTRY AND PHOTOPHYSICS OF ARYL BENZYL SULFOXIDES: α-CLEAVAGE AND THE ROLE OF THE SULFENIC ESTER[1]

A paper, a portion of which was published in the *Journal of Organic Chemistry*

Yushen Guo and William S. Jenks

Abstract: 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 from the solvent cage, leading to formation of diphenyl ethane 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 initial step is homolytic cleavage of a C–S bond, or α-cleavage.[2] 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 R-S-O-R'. The secondary chemistry of the sulfenic esters leads to other observed products.[3-8] Very modest yields of

sultenes (cyclic sulfenic ester) in some cyclic sulfoxide cases have been identified previously.[7,9,10] Quite recently, sultenes themselves were isolated in 45 - 67% yield after photolysis of a carbonyl-containing cyclic sulfoxide.[11] Examples of transformations in which the sulfoxide → sulfenic ester → products pathway has been proposed are shown in Figure 1.

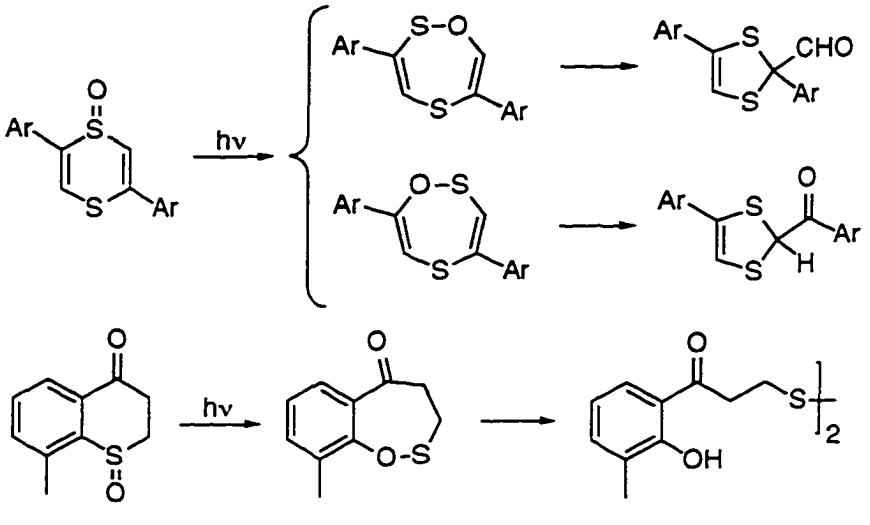


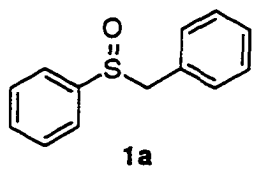
Figure 1. Examples of transformations which have been proposed to go through α-cleavage and sulfenic esters.

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 for acyclic sulfoxide structures strongly biased toward α-cleavage. We confirmed that the

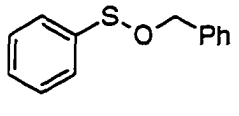
sulfenic esters are crucial intermediates in this chemistry, and also gave answers to several of these questions.

Results

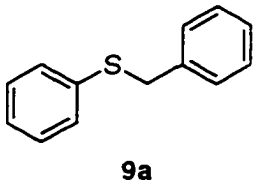
The UV absorption spectra of benzyl phenyl sulfoxide **1a** were obtained in different solvents (Figure 2). These results are consistent with the hypsochromic shift of the absorption maximum of DMSO in different solvents.[12] Assuming that the LUMO of the sulfoxide has an increased electron density at sulfur and a decreased electron density at oxygen compared with the HOMO, the shift is mainly due to stabilization of the sulfoxide ground state by hydrogen bond and other dipole interactions. Compared to its ketone analog, the sulfoxide absorption is blue shifted with a low energy limit of about 300 nm. This will affect the choice of both irradiation wavelength and photolysis reactor. Quartz reactors were used in order to achieve enough absorption by the sulfoxide.



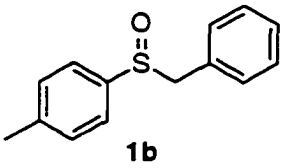
1a



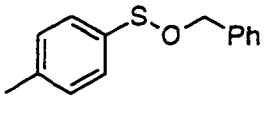
2a



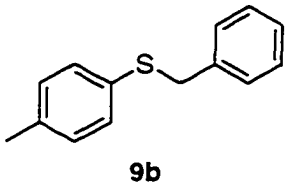
9a



1b



2b



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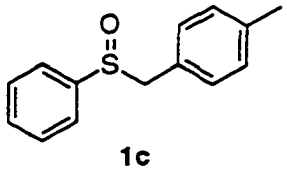
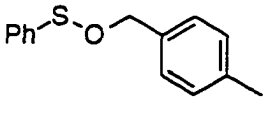
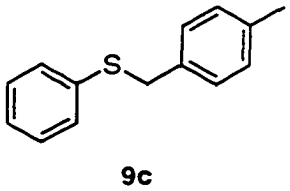


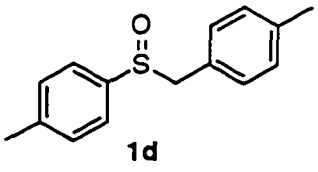
1c



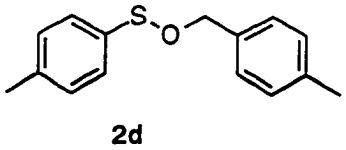
2c



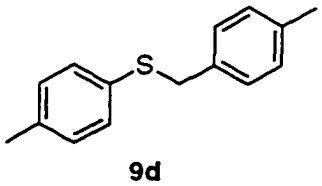
9c



1d



2d



9d

Photolysis of sulfoxides **1a-d**, 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 processes. Prolonged photolysis finally results in the appearance of insoluble precipitate (possible sulfur and polymers). Also, some of the sulfur-containing products appear to undergo complex redox equilibrium and/or scavenge oxygen which is introduced on workup and product analysis. Typical components of the mixture obtained in inert solvents are illustrated in Figure 3. To avoid the secondary photolysis problem, the reactions reported here were carried out to modest conversions, generally ≤20%. Starting concentrations for solution photolysis were all around 3-6 mM.

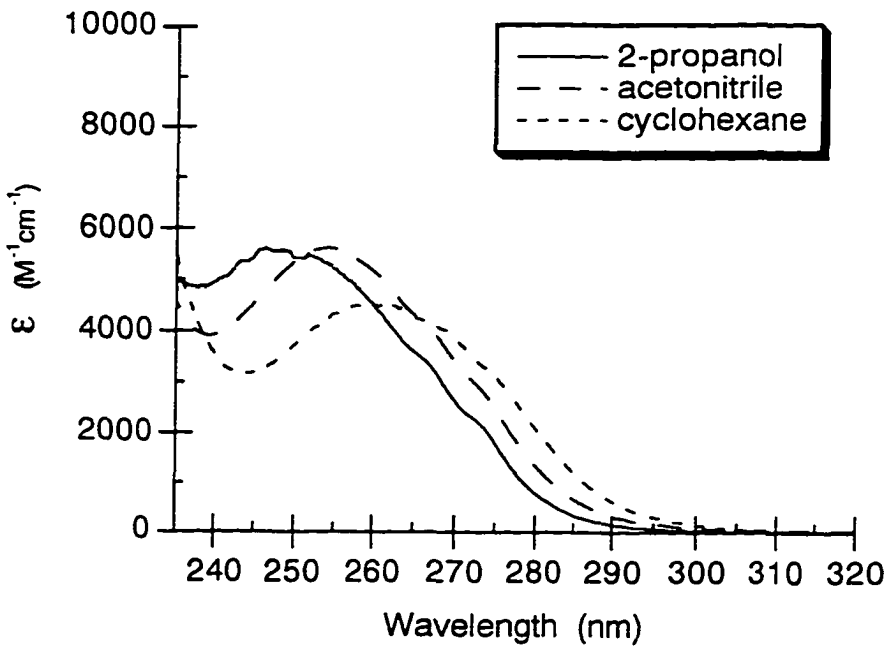


Figure 2. Absorption spectra of benzyl phenyl sulfoxide **1a** in different solvents. Notice the maximum in 2-propanol (248.5 nm) and the red shift in acetonitrile (6 nm) and cyclohexane (14 nm). This blue shift effect in polar solvent is very similar to the ketone n-π* state.

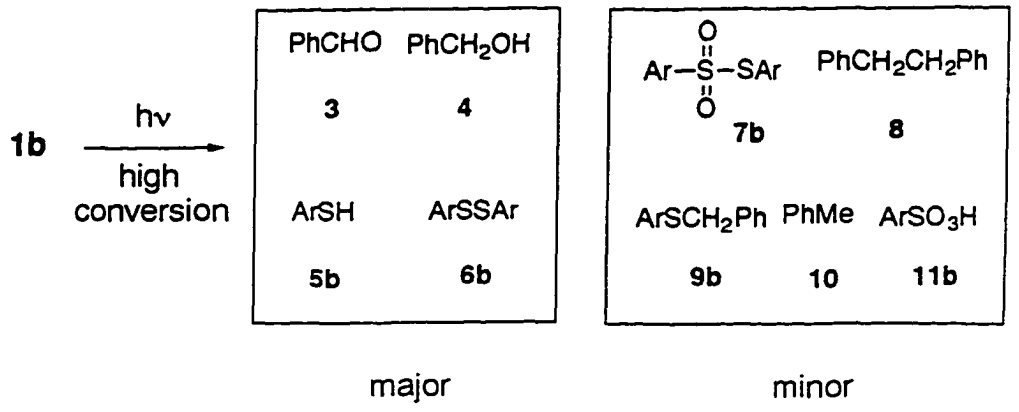


Figure 3. Observed products from extended photolysis of **1b** (Ar = *p*-tolyl).

Sulfoxides **1a-d** are particularly susceptible to secondary photolysis at lower energy wavelengths, as several of their photoproducts have larger absorption extinction coefficients at wavelengths above approximately 290 nm. In fact, early exploratory experiments on **1a** 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 **2a**, even at low conversion. The UV spectra of **1a**, **2a**, and some other major photolysis products are shown in Figures 4 and 5 for comparison. Independent synthesis of compounds **2a-d** showed that these sulfenic esters are stable enough for the analysis conditions. It also revealed the large difference in absorption coefficients for **1a-d** and **2a-d**. It became clear that compounds **2a-d** were probably formed, but were selectively photolyzed because of the excitation wavelength. This problem was alleviated by tuning to a more appropriate excitation wavelength. Photolyses in which the data of interest concerned the transformation of **1a-d** to **2a-d** were carried out using the output of a 150 W Xe lamp filtered through a monochromator which could be set to a more appropriate wavelength region, generally around 267±12 nm. Experiments concerned with the ultimate photoproducts were carried out using either the Xe lamp setup or the Rayonet photoreactor as indicated.

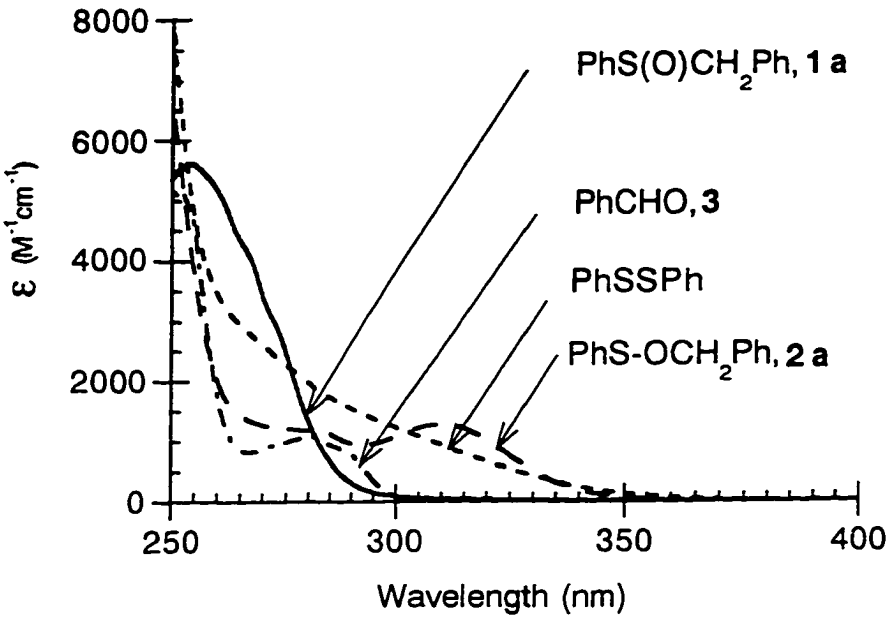


Figure 4. UV absorption spectra of benzyl phenyl sulfoxide **1a** and some major photolysis products in acetonitrile.

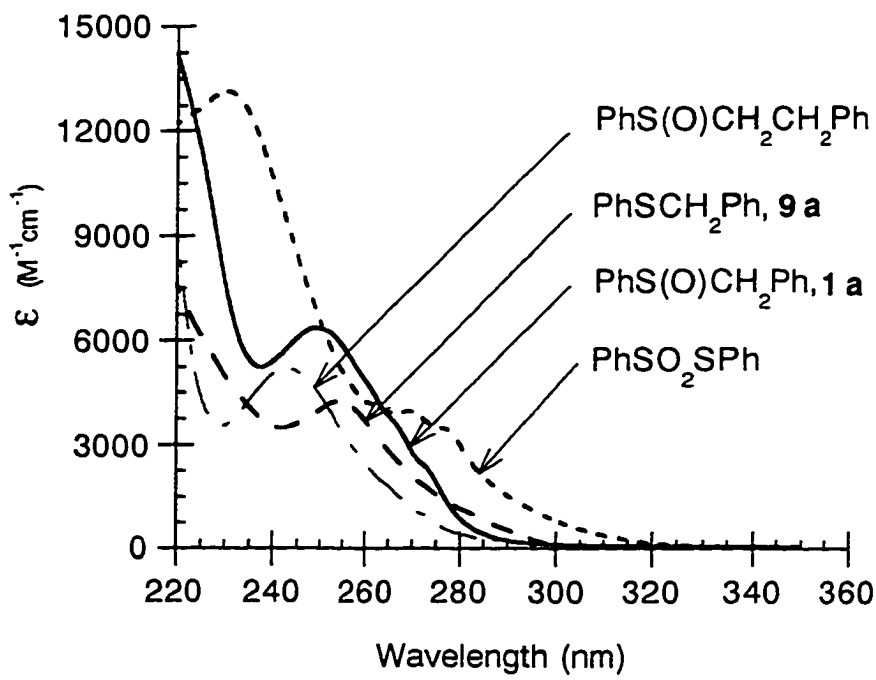


Figure 5. UV absorption spectra of benzyl phenyl sulfoxide **1a** and other related compounds in acetonitrile. Notice the change of sulfoxide absorption as the phenyl group moves from the α-position to the β-position.

The high yield of sulfenic esters was supported by the independent synthesis of these compounds. Although they are of low stability as reported before, we managed to get enough pure sample of one of the sulfenic ester and studied its absorption spectra and retention time which were identical to those we got from the HPLC trace. The UV absorption spectra are essentially independent of solvent (Figure 6).

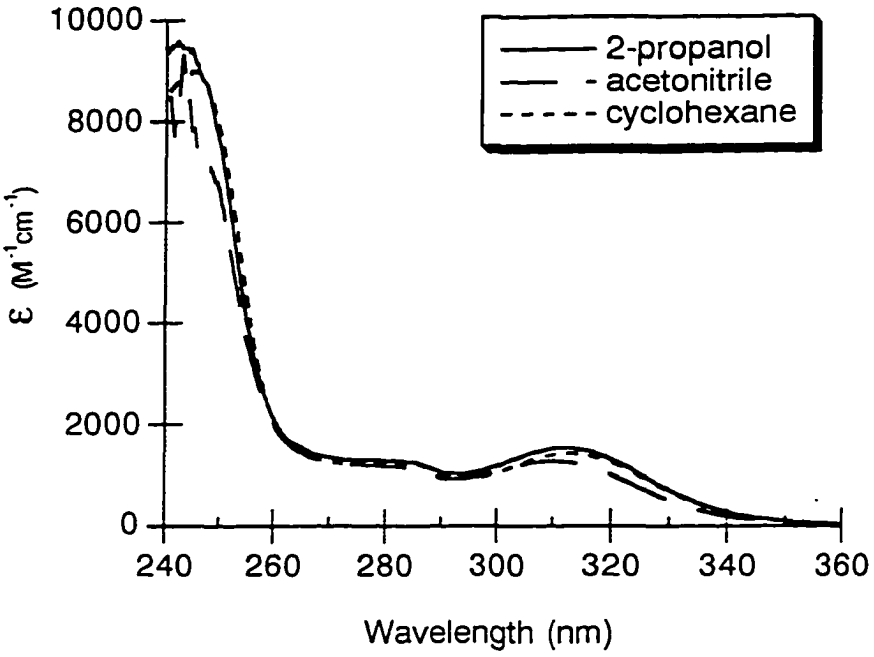


Figure 6. Absorption spectra of benzyl phenyl sulfenic ester (**2a**) in different solvents. Notice the absorption in the long wavelength region.

Exploratory photolysis of **1a** and **1b** was performed in several solvents using both the Rayonet and the Xe lamp/monochromator setup. We observed two kinds of solvent effects. 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. It has been reported that aldehydes can be trapped as their acetals, which are more photostable.[13] Acetal formation is probably induced by a trace of acid (e.g. $ArSO_nH$, n = 1-3)

formed during the photolysis and is not a photochemical process. Secondly, there was a 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 the viscosity was 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 a Rayonet. Only **3**, **5b**, and **6b** were observed as products. This phenomenon is illustrated by the product distributions given in Table 1. The trends in these data are much more important than the precise numbers, since the latter are very dependent on excitation conditions and conversion. It should also be pointed out that we view the relative quantities of **5b** and **6b** given in Table 1 and elsewhere in this paper with extreme caution. We did not take extreme measures to exclude oxygen from our reactions and analysis solvents and the amount of **5b** reported is quite likely underestimates of the "true" value, while the amount of **6b** is overestimated. Indeed, control experiments subjecting dilute solutions of **5b** to our standard handling and analysis conditions showed some conversion to **6b**.

C-18 reverse phase HPLC was intensively used to monitor the photolysis reactions, both qualitatively and quantitatively. Because the photolysis products have a wide range of polarity, gradient eluent was used in order to save time and also get satisfactory separation. Figure 7 is a typical HPLC run.

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 in Table 1. One possible reason for a lower arylsulfinyl portion is because we did not quantitatively account for the production of arylsulfinic and arylsulfonic acids. They are not separated very well by reverse phase HPLC due to similar high polarities.

Given the solvent reactivity and viscosity effects, 2-methyl-2-propanol, spiked with 1%

Table 1. Product distributions from photolysis of **1b** to modest conversions in several solvents.

Solvent	Conversion (%)[a]	Relative Product Yields[b]						
		2b	**3**	**4**	**5b**[c]	**6b**	**7b**	**8**
2-methyl-2-propanol[c]	5	100						
2-methyl-2-propanol[c]	15	74	11	6		5	4	
acetonitrile	7	72	6				19	9
acetonitrile	24	73	6			2	12	7
acetone	5		33	9		3	23	33
acetone	20		32	17		4	17	30
neat (KBr)[d]	5		50		45	5		
neat (77 K)[d]	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 percent. Other trace products are not included in the table. A Xe lamp with monochromator set to 267 nm was used for irradiation unless otherwise noted. (c) 1% water added. (d) No internal standard used. Conversion estimated by comparison of product integrations to total. Excitation provided by Rayonet 300 nm bulbs.

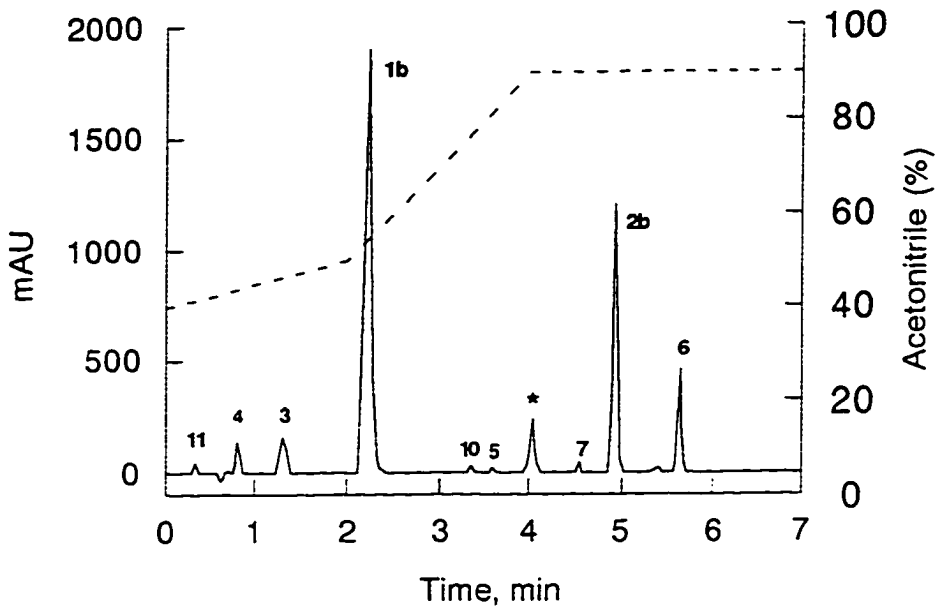


Figure 7. Typical reverse phase HPLC chromatograph of the photolysis of **1b** (* *p*-xylene used as internal standard).

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 of the photolysis of **1b** in 2-methyl-2-propanol as a function of time is shown in Figure 8, which also illustrates a single quantitative description of the product mixture. The most valuable information is that the initial product from photolysis of **1b** is almost exclusively the sulfenic ester **2b**. Products, such as benzaldehyde and disulfide **6b**, are clearly a result of a secondary photochemical event.

Since the appearance of products, such as benzaldehyde and thiophenol, were determined to be multiphoton events, the meaningful quantum yields are those for the loss of starting sulfoxides **1a-d** and the formation of the sulfenic esters **2a-d**. Though compounds **2a-d** were amenable to analysis, particularly by reverse phase HPLC, we were unable to obtain macroscopic samples of these materials in purity higher than about 90%. The difficulty in handling benzenesulfenic esters has been noted by other authors.[14] Various methods for

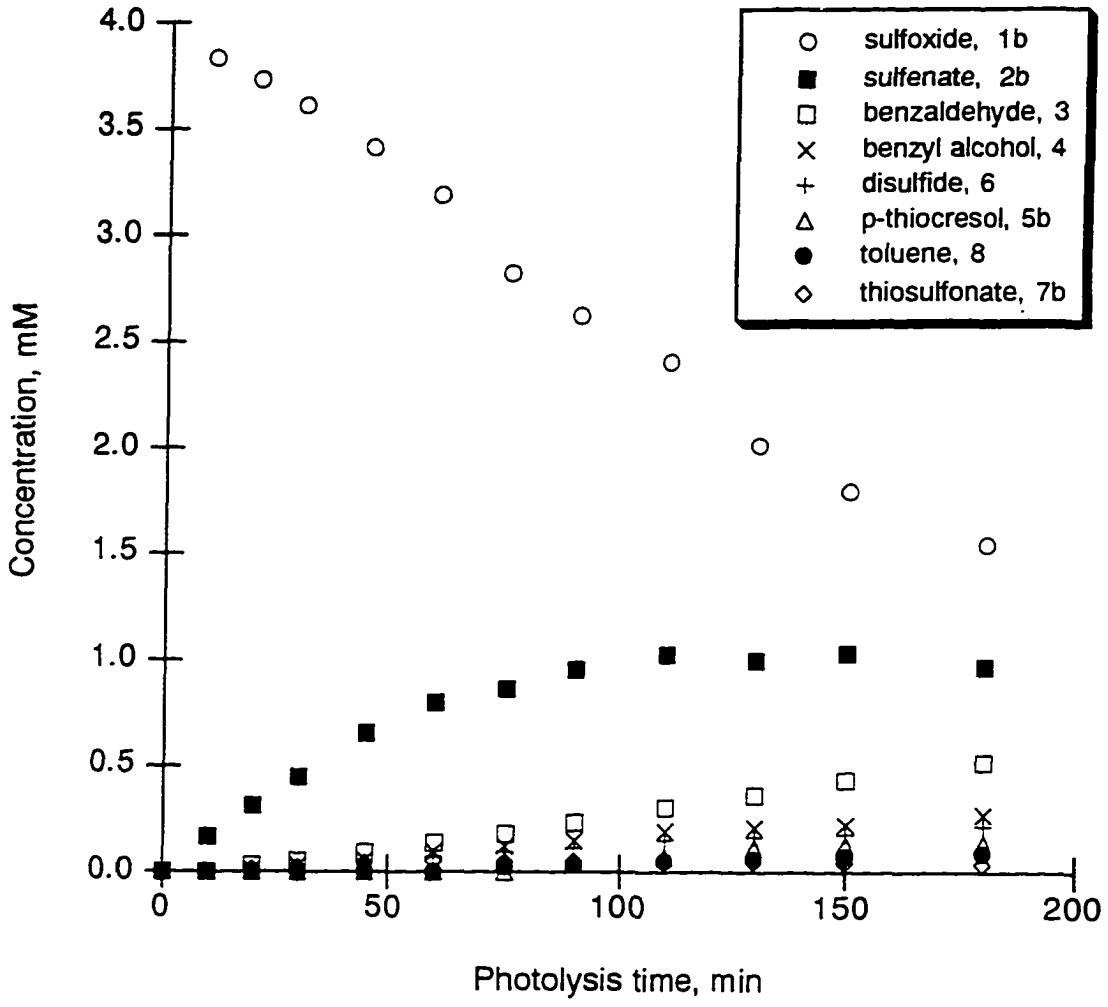


Figure 8. The reaction mixture as a function of photolysis time for a solution of **1b** in 2-methyl-2-propanol, using light centered at 267 nm. Note that for photolysis times up to *ca.* 30 minutes, sulfenic ester **2b** is virtually the sole product. Points are averages of at least two HPLC determinations.

purification always led to decomposition such that the total purity was difficult to improve beyond that which was obtained from the crude synthetic reaction mixture and further vacuum distillation. Though we felt comfortable using calibration curves for this material from Figure 8, it was decided to measure the quantum yield of the 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 products 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. Effective stirring during photolysis is very critical for quantitative measurements,

Table 2. Quantum yields for disappearance of starting materials.[a]

Compound	Solvent	Wavelength[b]	Φ_{loss}[c]	Φ_{rot}[d]
1a	acetonitrile	267 nm	0.28	
1b	acetonitrile	267 nm	0.29	0.53
1b	2-propanol	267 nm	0.30	0.44
1a	2-methyl-2-propanol	267 nm	0.20	
1b	2-methyl-2-propanol	267 nm	0.21	0.42
1b	acetone	267 nm	0.33	0.41
2a	2-methyl-2-propanol	313 nm	0.69	

(a) All solutions were originally 4-6 mM in starting material and were flushed with Argon 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}.

such as the product distribution and quantum yield, mainly because of the internal filter effect which affects secondary photolysis. Without stirring, the quantum yield for the disappearance of sulfoxide is about 1/3 to 1/2 of those with stirring, although other conditions were the same.

The optical activity of sulfoxides 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 **1a** and **1b** (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) (*R*)-(+)-**1b** was prepared by standard literature methodology.[15] 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 conversion* were attributed to partial racemization of **1b**, as is discussed below. The quantum yields for total loss of rotation, Φ_{rot}, are given in Table 2.

In view of the sub-unity quantum yields for the disappearance of sulfoxides and product formation, it appeared likely that cage and/or non-cage recombination of sulfinyl and benzyl radicals occurs. In order to assess the extent of non-cage recombination, double label experiments were carried out in order to gain further evidence for radical pairs as intermediates (Figure 9). 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 bibenzyl. 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 about 7% of the loss of starting materials. Cross sulfenic esters **2a** and **2d** were also observed, each

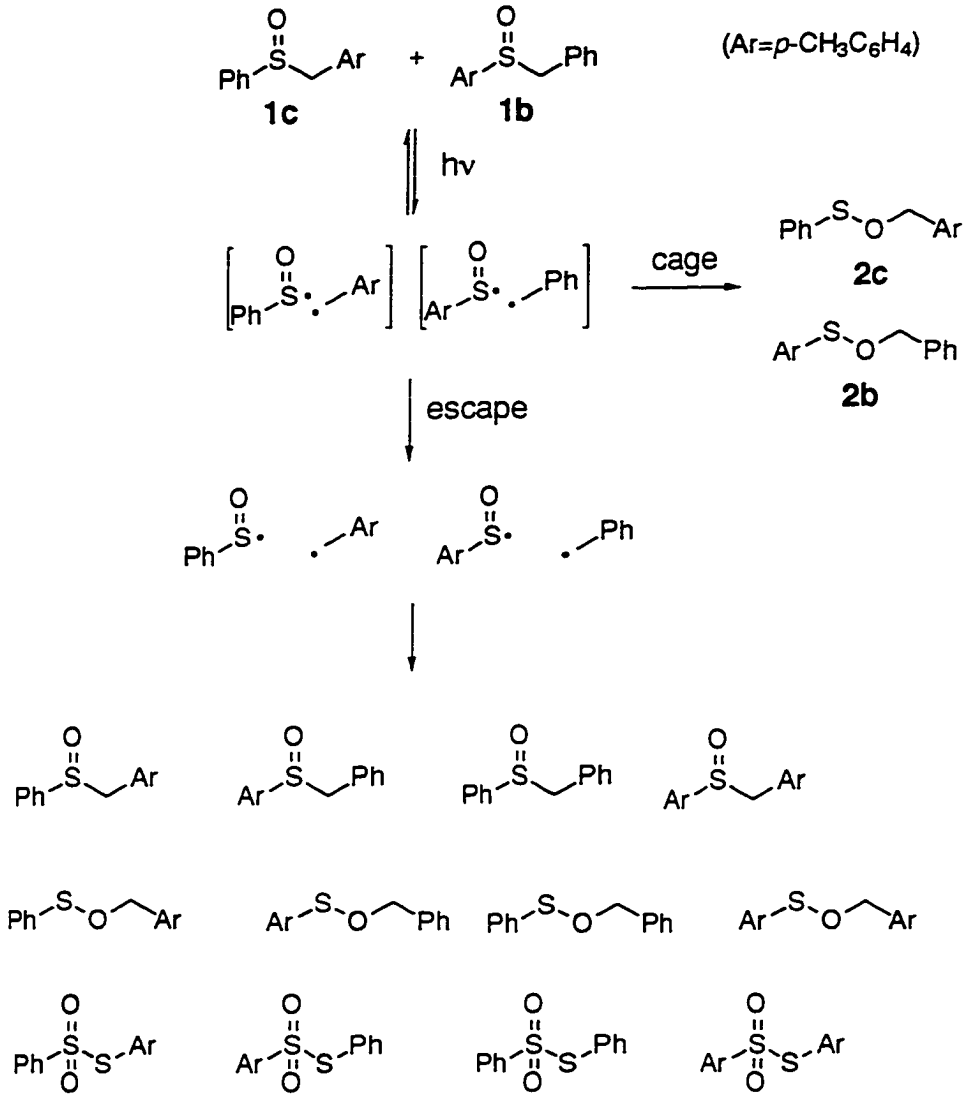


Figure 9. Cross label photolysis of **1b** and **1c** mixture.

accounting for about 6% 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 40% of lost starting materials.

In reference to the cage effect definition by Turro and coworkers[16] in the study of dibenzyl ketone and related compounds, we define the "cage effect" in term of the concentrations of sulfenic ester products according to the following equation.

$$\text{Cage effect} = \frac{[\text{Cage Products}] - [\text{Escape Products}]}{[\text{Cage Products}] + [\text{Escape Products}]}$$

The results shown in Table 3 indicate that in most solvents except acetone, the efficiency of crossover sulfoxide formation is comparable to that for sulfenic ester formation. This result is consistent with the claims of recombination with racemization.

Table 3. Quantum yield of cross label experiments and cage effects in different solvents.

Solvent	$PhS(O)CH_2Ph$ ($ArS(O)CH_2Ph$)	$PhS\text{-}OCH_2Ph$ ($ArS\text{-}OCH_2Ar$)	$PhS\text{-}OCH_2Ar$ ($ArS\text{-}OCH_2Ph$)	Cage Effect (%)
t-BuOH	≤ 0.0010	≤ 0.0010	0.08	≥ 98[a]
2-Propanol	≤ 0.0015	≤ 0.0015	0.12	≥ 98[a]
Acetonitrile	0.01	0.01	0.11	85[a]
Acetone	0.04	0	0	b,c

(a) Calculated only from sulfenic ester products. The effects of bibenzyls and thiosulfonates, which are negligible compared to other products under the photolysis conditions, are not considered. (b) The quantum yields of $PhCH_2CH_2Ph$ and $ArCH_2CH_2Ar$ are 0.017 each; $ArCH_2CH_2Ph$ is 0.033. (c) Because the sulfenic esters are not detected, the cage effect must be very small (near zero).

Direct photolysis of compounds **2a-b** yields product mixtures very similar to those found on extended photolyses of **1a-b**. Generally, the photolysis of the sulfenic ester at different wavelengths gave the same products and similar product ratios. The yield of products from the aryl sulfur part at lower wavelength were slightly lower than those at higher wavelength. The reason was that the sulfur-containing products (e.g. thiophenol) were more liable to secondary photolysis at lower wavelength UV irradiation. By intentionally carrying out photolyses of **2a-b** at higher wavelengths, where the extinction coefficients of **1a-b** are very low, the selective photolysis of sulfenic esters can be achieved without affecting any sulfoxide which may have been formed (Figure 10). Significantly, no sulfoxide, bibenzyl (**8**) and thiosulfonate (**7**) were observed; only products deriving from S-O bond cleavage were found.

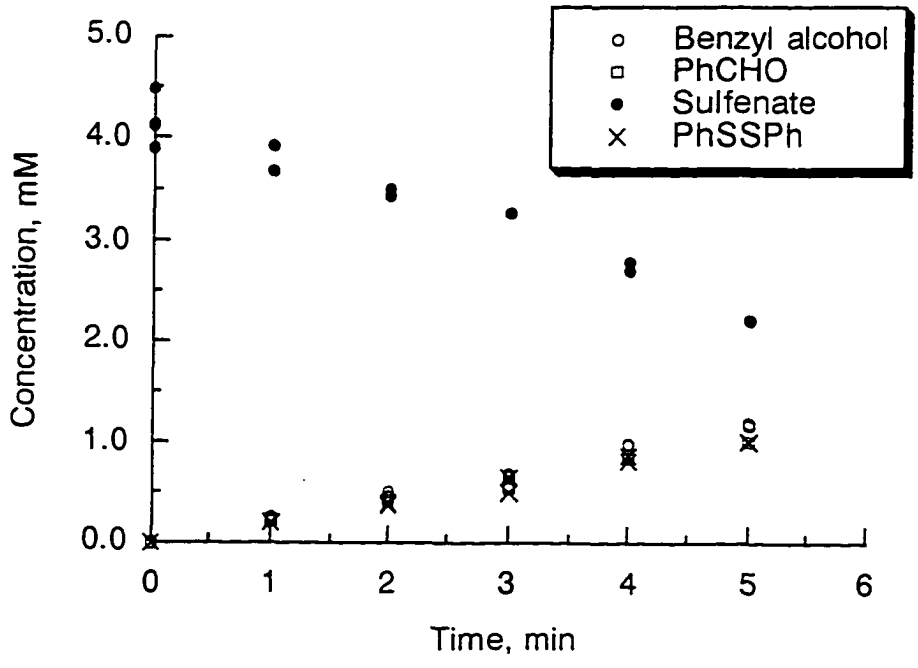


Figure 10. Photolysis of benzyl phenyl sulfenic ester PhS-OCH_2Ph (**2a**) in *tert*-butyl alcohol at 313 nm. The photolysis of **2b** gave similar results.

The triplet energies of alkyl phenyl sulfoxides are relatively high. Very similar phosphorescence spectra were obtained for **1a-b** as for phenyl methyl sulfoxide[15], which led us to estimate a triplet energy of about 80 kcal/mol. 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 to be the mechanism for energetic reasons.[3,17-21] 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 **7a-b** and **8**, as seen in Table 1. The apparent quantum yields Φ_{loss} and Φ_{rot} in acetone are shown in Table 2.

The acetone triplet effect has been shown clearly in both product distribution (Table 1) and cross label experiments (Table 2). Another most significant observation is the absence of sulfenic esters **2a-d** in the photolysis of sulfoxides **1a-d** in acetone. We hypothesize that triplet energy transfer from acetone to **1a-d** may be endothermic by as much as 2-3 kcal/mol, given the triplet energies of related sulfoxides, and thus relatively slow.[22] (Self-quenching by acetone is almost insignificant.[23]) On the other hand, the absorption spectrum of **2a** makes it self-evident that energy transfer from acetone ($E_T \approx 79$ 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 assumption by irradiating solutions containing nearly equal amounts of both **1a** and **2a** in acetone. The starting concentration of each compound was 4-5 mM. About 90% of the light is absorbed by acetone as estimated from the extinction coefficients, although the optical density of the sulfoxide **1a** is about three times of that sulfenic ester **2a** at the excitation wavelength (267 nm). The concentrations of both materials were monitored as a function of photolysis time until **2a** was about 30% consumed. Within experimental error, the

concentration of sulfoxide was identical to its original value (Figure 11). Also, the products from this photolysis are almost identical to those when sulfenic ester **2a** is directly photolyzed.

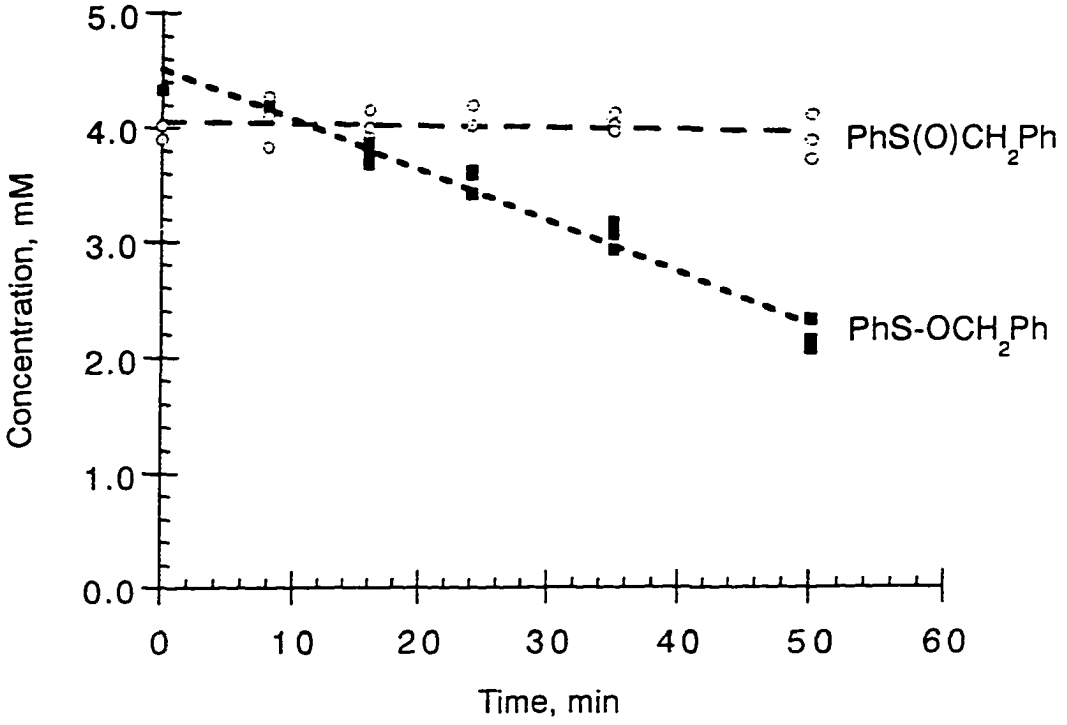


Figure 11. Photolysis of benzyl phenyl sulfoxide **1a** and sulfenic ester **2a** mixture in acetone at 267 nm.

Oxygen has been widely used as a triplet quencher in the study of photochemistry and photophysics of arene and ketone systems. It also reacts with carbon-centered radicals very quickly. We studied the photolysis of **1a** in benzene solutions (4 mM) with and without oxygen at 294 nm with conversion under 15% (Table 4).

We can see that oxygen caused a much higher quantum yield of sulfoxide disappearance, but had almost no effect on the production of benzaldehyde, which probably comes from the secondary photolysis of the sulfenic ester. It is likely that oxygen reacted with escaped radicals and caused the increase of quantum yield. It is also observed that in the

Table 4. Oxygen effect on the quantum yields of sulfoxide and benzaldehyde.

Φ	Oxygen Saturated	Argon Saturated
$PhS(O)CH_2Ph$	0.39	0.17
PhCHO	0.15	0.15

presence of oxygen, the benzyl alcohol yield decreased and some benzoic acid and benzenesulfonic acid products were also detected. This suggests that in the presence of oxygen, the initially formed radicals are partially captured. This is supported by a laser flash photolysis study of related sulfoxides.[24]

Isoprene is a widely used triplet quencher with a triplet energy about 60 kcal/mol. Argon-flushed solutions containing sulfoxide, a known concentration of internal standard, and various concentrations of diene were irradiated in parallel at defined wavelength. Relative quantum yields were determined by GC analysis. A study of the photolysis of sulfoxide **1a** in both benzene and acetonitrile gave similar results: isoprene can quench the production of PhCHO, but also increases the quantum yield of starting sulfoxide disappearance. Also, in the presence of isoprene, less $PhCH_2OH$ was observed. The reason for this "reverse-quench" may be that the non-cage radicals, such as $PhS(O)^{\bullet}$ and $PhCH_2^{\bullet}$, react with the isoprene double bond to form the radical addition products giving rise to an inefficient chain process which destroys sulfoxide. Another possibility is the formation of a sulfoxide-alkene complex which may lower the excitation energy.

Discussion

Mechanism of sulfenic ester formation

The nearly quantitative formation of sulfenic ester **2b** on photolysis of **1b** is documented in Figure 8. Because of the apparent generality in sulfoxide photochemistry, it is

important to consider various mechanisms for the transformations of **1a-d** to **2a-d**. 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 coworkers.[25,26] 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 12(a). Random recombination leads to loss of configuration at both the sulfur atom and the CH_2 at equal rates (chiral ArS(O)CHDPh was used). However, it was also concluded that the reversible thermal rearrangement of **1b** and **2b** does *not* pass through a radical pair intermediate. This idea is based largely on a small, negative activation entropy.[25] 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. Formation of **2b** in its excited state by photolysis of **1b** would be expected to behave very much like the direct photolysis of **2b**, but is not observed: only **2b** is formed during the initial stage of photolysis of **1b** in 2-methyl-2-propanol. Benzaldehyde and thiophenol are *two* photon products of sulfoxide photolysis. In the event, adiabatic rearrangement shown in Figure 12(c) can be eliminated as a significant pathway.

The non-adiabatic rearrangement of **1b** to **2b**, shown as Figure 12(b), 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.[27]) Furthermore, the observation **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 solvents. 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.[27-29] For these reasons, we believe that simple α-cleavage and reclosure is the best explanation for the formation of **2**. 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.

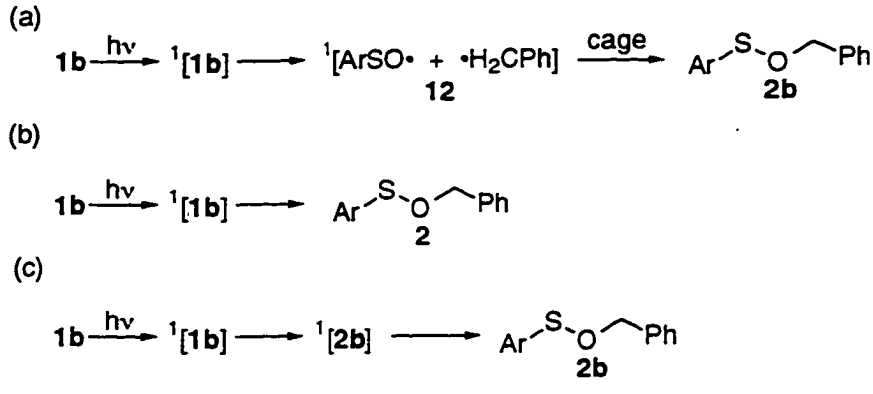


Figure 12. Possible mechanisms for the transformation of sulfoxides to sulfenic esters, using **1b** → **2b** as the example.

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 *ortho*-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. Although this process cannot be ruled out, it should be a minor process compared to the major α-cleavage pathway.

As pointed out before, reactions rationalized by formation of sulfenic esters represent only a subset of those which are best explained by α-cleavage.[18,30-36] 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, which is consistent with our observations.

Excited state multiplicity

Characterization of the multiplicity of the excited states is very important to predict photochemical reactions, as shown in the development of the photochemistry of most of the well-understood functional groups.[38] There is very limited knowledge about the excited state multiplicity of sulfoxides (including lifetime and energy),[22] especially in solutions at room temperature. The photoreactivities of aromatic sulfoxides have been attributed to their triplet states, mainly by using the ordinary criteria of triplet sensitization and quenching experiments.[2,19,37] According to Kasha's rule,[39] we can assume that only the vibrationally equilibrated lowest excited state of a given multiplicity will be involved in the primary photochemical and photophysical process of the sulfoxide molecules. We will only consider the lowest triplet (T_1) and lowest singlet state (S_1).

The multiplicity of the reactive excited state is of considerable importance in photochemical α-cleavage processes. It has been proved that the lowest triplet state of dialkyl ketones is much more reactive toward α-cleavage than the singlet state.[40] We assign the reactive states of **1a-d** to be a singlet based both on the very high yields of **2a-d**, which represents geminate recombination, and the sharp contrast that is drawn between photolysis in acetone and other solvents. From Table 2, we can see a significant cage effect in 2-methyl-2-propanol and 2-propanol. The cage effect decreased dramatically in solvents of lower viscosity. In contrast, much larger proportions of the escape products **7b** and **8** are observed in acetone, although the viscosity of acetone and acetonitrile are within 5% of each other at room temperature. Because the sulfenic ester is not directly observed (*vide infra*), a cage effect cannot be calculated, but it is certainly small. Also, Φ_{rot} is much closer to Φ_{loss} in acetone than in acetonitrile. The result is interpreted to mean that a smaller percentage of molecules which cleave undergo geminate recombination. This observation is consistent with a triplet reaction in

acetone and singlet cleavage in other solvents. However, we cannot rule out a mixture of singlet and triplet cleavage. It was observed that Φ_{loss} is not decreased (but increased) by the presence of oxygen. We also tried other triplet quenching agents (*e.g.*, isoprene or other dienes) at both lower (254 nm) and higher (294 nm) wavelength. The inability to quench the sulfoxide by the triplet quenchers indicates that α-cleavage is unlikely to form from a triplet state, at least not predominantly.

Quantum yields of α-cleavage

If the excited states of **1b** were racemic or had a very low barrier for inversion, we would expect the quantum yield for loss of optical activity, Φ_{rot}, to be approximately unity. As the observed values of Φ_{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 **2b** or may return to starting material **1**, with at least partial racemization. Therefore, we may use the observed values of Φ_{rot} and Φ_{loss} to estimate the quantum yield of α-cleavage. The difference between Φ_{rot} and Φ_{loss} for (*R*)-(+)-**1b** is attributed to sulfinyl-benzyl radical pairs **12** which reverted to **1b**. 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 Φ_{rot} is identical to the quantum yield for cleavage, Φ_{cleave}.

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

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

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 Φ_{rot}.

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

The observed value of Φ_{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 (*S*)-sulfoxide and **2b** are negligible. An interesting, but not surprising, conclusion which can be drawn is that regioselectivity of recombination of the radical pair **12** is clearly kinetically controlled by an early transition state, given that the sulfoxide/sulfenic ester equilibrium generally lies quite far to the side of the sulfoxide.

Photolysis of benzyl arenesulfenic esters

Photolysis of sulfenic ester **2a** at different wavelengths gave similar products, but in different ratios. In all cases, no corresponding sulfoxide **1a** was detected. Quantitatively, the arylsulfinyl part was more likely out of balance at shorter rather than at longer wavelength. This is expected because of the higher energy of the short irradiation wavelengths, which causes insoluble sulfur or polymer products. The main reason that the sulfenic ester can survive short wavelength irradiation in the photolysis of sulfoxides is the screening effect of sulfoxides. As 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 (Figure 13). Any accumulated **5a** may act as an active hydrogen atom donor for escaped benzyloxy radicals, along with other species. Formation of **6a** 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 (Argon flushing), the analyses were not, and some **5a** may have converted to **6a** at that point as well.

Photolysis of **1b** at 300 nm in the solid state provides an example of *in situ* preparation of **2b**, 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

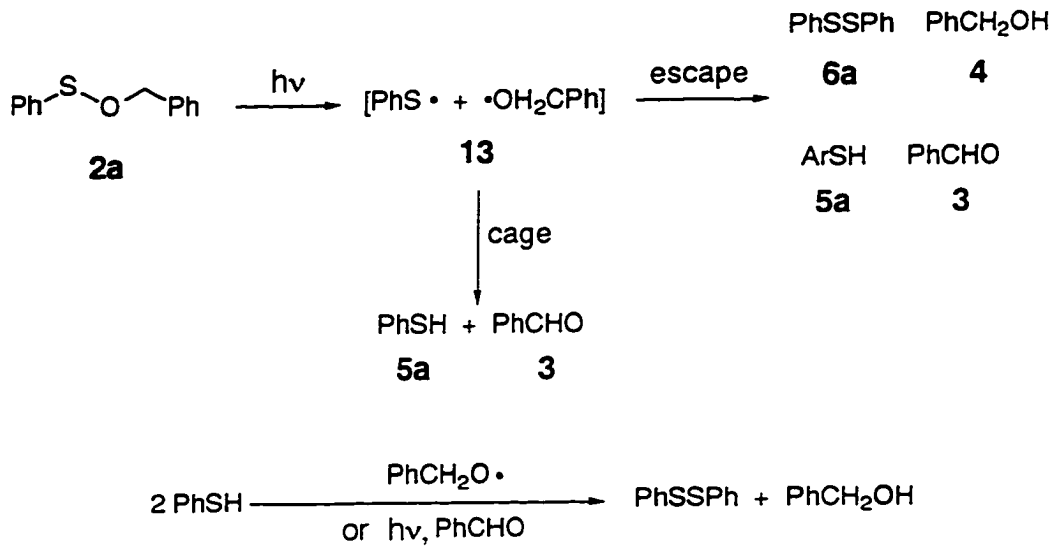


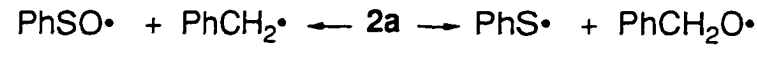
Figure 13. Photolysis of sulfenic ester **2a** and formation of products.

these cases is within experimental error of a 1:1 ratio of "benzyl" and "sulfinyl" products, represented by **3** and (**5b** + **6b**). We take the small quantity of **6b** to be an artifact of subsequent oxidation during handling.

The assignment of the multiplicity of the reactive state of **2a-d** is less definite than for **1a-d**. 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*-nitrobenzene sulfenic esters,[14,41-43] and has concluded that the chemistry is triplet-based. While this is quite possibly true here as demonstrated by our product distribution analysis, it should be recognized that the nitro group has a strong perturbation on the chromophore which also has important effects on the observed chemistry.

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,[44] benzyl,[45] phenylthiyl,[45] and phenylmethoxyl (estimated using the Benson tables in the literature)[46] are all either experimentally known or can be reliably estimated to within a few kcal/mol by Benson additivity methods.[47] 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 of the relevant species are known for the homolysis of methyl methanesulfenic ester by either S–O or O–CH_3 cleavage[44,45,48] and the latter is thermochemically favored by about 17 kcal/mol. Despite this, it is known that photolysis of *t*-butyl methanesulfenate also proceeds by S–O cleavage.[49] *Ab initio* computations at the 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 arylsulfenic ester 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.[49]



ΔH_f (kcal/mol)	13.0	49.0	54.9	28.1

Summary

The data presented in this chapter make a very strong case that the photolysis of aryl benzyl sulfoxides proceeds through the mechanism outlined in Figure 14. The primary process is cleavage of the S–CH_2 bond 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 **1a-d** is carried out using well-chosen wavelengths

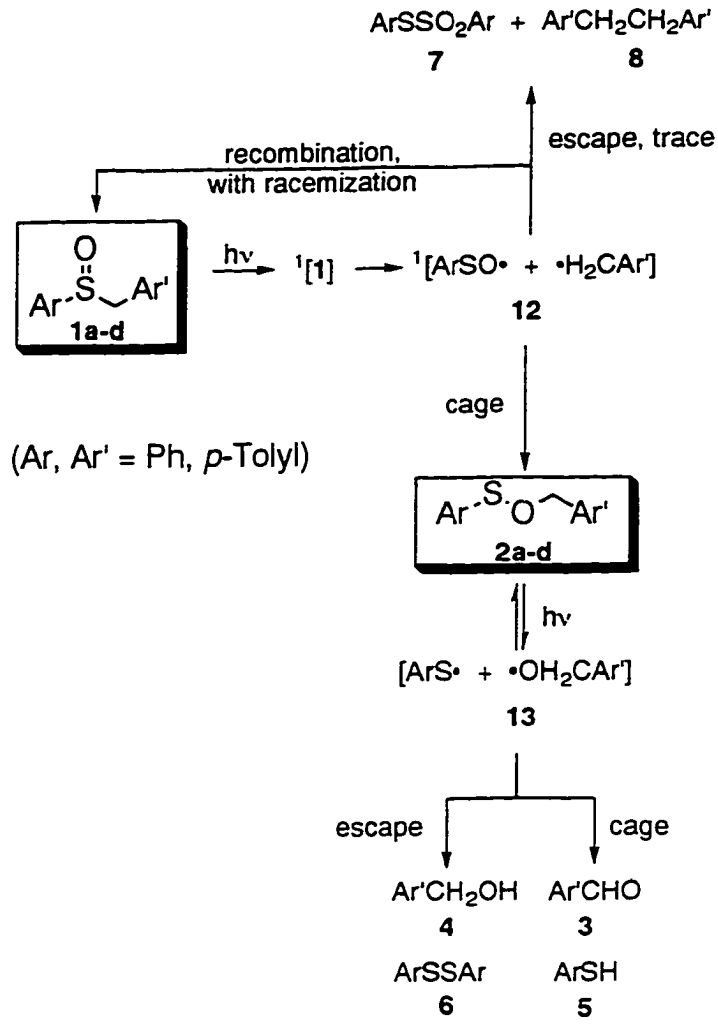


Figure 14. Proposed overall reaction scheme for photolysis of **1a-d**.

(*i.e.*, <280 nm) and solvents (*e.g.*, 2-methyl-2-propanol), **2a-d** and **1a-d** (with inversion of configuration at sulfur) are the nearly exclusive products up to reasonable conversion. Using longer wavelength light results in selective photolysis of **2a-d** so that other products (*i.e.*, **3-6**) *appear* to be primary. Based on 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 **2a-d** 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 germinal cage are quite competitive.

In summary, the photolysis of **1a-d** follows the previously proposed sulfoxide → sulfenic ester → products pathway,[2] 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 **2a** does not form **1a**. Racemization is believed to result from recombination of the geminate radical pair which partitions between formation of **2a-d** and reversion to (racemic) **1a-d**. 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, spectral 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 are 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 ODS Hypersil reverse phase column (5 μm, 200 x 2.1 mm, Hewlett Packard) 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_2O_2 in methanol.[49,50] Phosphorescence spectra were obtained as described previously.[21] (*R*)-(+)Benzyl *p*-tolyl sulfoxide was prepared by reaction of benzyl magnesium bromide with the corresponding menthyl *p*-toluenesulfinate.

Sulfenic esters **2a** and **2b** were prepared by reaction of benzyl alcohol (or *p*-methylbenzyl alcohol) with the corresponding sulfenyl chloride.[24] The sulfenyl chlorides were prepared from sulfuryl chloride and disulfides according literature method.[51] 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 sulfenic ester peaks in the HPLC traces.

Product identifications. Product identification was based on comparison to genuine samples in chromatographic behavior.[52,53] 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 spectral 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 sulfenic esters **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 UV absorption 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

Table 5. Melting point, ^{1}H NMR, and ^{13}C NMR data of **1a-1d** and **9a-9d**.

Compounds	mp (°C)	^{1}H NMR (δ, ppm)	^{13}C NMR (ppm)
9a	42–43	4.15 (s, 2 H), 7.21–7.40 (m, 10 H)	39.1, 126.4, 127.3, 128.6, 129.0, 129.8, 129.9, 136.5, 137.6
1a	139–140	3.96 (d, J = 12.6 Hz, 1 H), 4.06 (d, J = 12.6 Hz, 1 H), 7.20–7.73 (m, 10 H)	63.5, 124.4, 128.2, 128.4, 128.8, 129.1, 130.3, 131.1, 142.7
9b	43–44	2.33 (s, 3 H), 4.09 (s, 2 H), 7.09 (d, J = 8.1 Hz, 2 H), 7.24 (d, J = 8.1 Hz, 2 H), 7.26–7.31 (m, 5 H)	21.2, 39.9, 127.2, 128.5, 128.9, 129.7, 130.8, 132.6, 136.7, 137.9
2b	139–141	2.39 (s, 3 H), 3.96 (d, J = 12.5 Hz, 1 H), 4.09 (d, J = 12.5 Hz, 1 H), 6.98–7.29 (m, 5 H)	21.5, 63.8, 124.5, 128.3, 128.5, 129.4, 129.6, 130.4, 139.7, 141.7
9c	67–68	2.34 (s, 3 H), 4.11 (s, 2 H), 7.11 (d, J = 8.0 Hz, 2 H), 7.21 (d, J = 8.0 Hz, 2 H), 7.19–7.35 (m, 5 H)	21.2, 38.8, 126.3, 128.8, 128.9, 129.3, 129.7, 134.4, 136.7, 136.9

Table 5.

(continued)

3c	99–100	2.31 (s, 3 H), 3.96 (d, J = 12.6 Hz, 1 H), 4.07 (d, J = 12.6 Hz, 1 H), 6.87 (d, J = 8.1 Hz, 2 H), 7.06 (d, J = 8.1 Hz, 2 H), 7.35–7.50 (m, 5 H)	21.1, 63.3, 124.3, 126.0, 128.7, 129.1, 130.2, 131.0, 138.0, 142.9
9d	58–61	2.32 (s, 3 H), 2.33 (s, 3 H), 4.06 (s, 2 H), 7.08 (d, J = 7.8 Hz, 2 H), 7.10 (d, J = 8.1 Hz, 2 H), 7.18 (d, J = 7.8 Hz, 2 H), 7.23 (d, J = 8.1 Hz, 2 H)	21.1, 21.2, 39.5, 128.8, 129.2, 129.7, 130.6, 132.8, 134.7, 136.5, 136.8
4d	132–133	2.31 (s, 3 H), 2.39 (s, 3 H), 3.92 (d, J = 12.6 Hz, 1 H), 4.04 (d, J = 12.6 Hz, 1 H), 6.88 (d, J = 8.0 Hz, 2 H), 7.05 (d, J = 8.0 Hz, 2 H), 7.22 (d, J = 8.1 Hz, 2 H), 7.28 (d, J = 8.1 Hz, 2 H)	21.3, 21.5, 63.6, 124.6, 129.3, 129.6, 130.3, 130.8, 138.1, 139.9, 141.6

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 argon flushing to remove oxygen. 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 hour 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 di-*p*-tolyl disulfide were observed in a 1.0 : 0.9 : 0.1 ratio.

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 argon under a septum. The pellet was irradiated in the Rayonet with 300 nm bulbs for 1 hour. The pellet was crushed and extracted several times with acetonitrile. The resulting solution was analyzed by HPLC. Conversion was about 5%. Benzaldehyde, *p*-thiocresol, and di-*p*-tolyl disulfide were observed in a 1.0 : 0.85 : 0.1 ratio.

Quantum yields. Quantum yields were determined using the PTI lamp. The actinometer was azoxybenzene.[54] 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.[56] Full geometry optimization was used at the RHF/6-31G(d,p) level. 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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(1) Most of the results in this chapter were published in *J. Org. Chem.* **1995**, *60*, 5480-5486, and are reproduced with permission from the American Chemical Society. ©Copyright 1995 American Chemical Society.

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CHAPTER III

PHOTOLYSIS OF BENZYL 2-NAPHTHYL SULFOXIDE

A paper prepared for *Tetrahedron Letters*

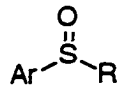
Yushen Guo and William S. Jenks

Abstract: The photolyses of the title compound in acetonitrile and acetone solution are described. The results support the α-cleavage mechanism as the main photochemical process. Homolytic cleavage forms naphthylsulfinyl/benzyl radical pair which gives sulfenic ester as the primary product. With acetone as triplet sensitizer, the primary radical pair undergoes significant escape, leading to formation of corresponding thiosulfonate and bibenzyl. Secondary photolysis is affected by irradiation wavelength. Deoxygenation was also observed for this sulfoxide in both solution and solid state. 2-Naphthylsulfinyl radical was directed observed from laser flash photolysis of the sulfoxides. Quantum yields and other mechanistic observation are discussed.

Introduction

We have studied the photochemistry of benzyl phenyl sulfoxide and other alkyl aryl sulfoxides **1**, which show α-cleavage as the primary process. The corresponding sulfenic ester is the most important intermediate whose fate depends on solvent, irradiation wavelength and the structure of the sulfoxides. In order to further this study, especially to red shift the excitation wavelength of the starting sulfoxide, we synthesized benzyl 2-naphthyl sulfoxide **2** and studied its photochemistry in comparison with benzyl phenyl sulfoxide. Red shifting of the absorption is desirable on two counts: (1) any synthetic application for this chemistry is improved if a lower energy light source can be used. (2)

Mechanistic study by laser flash photolysis is also made easier by extension of the absorption to higher wavelength to decrease interference from other species.



1

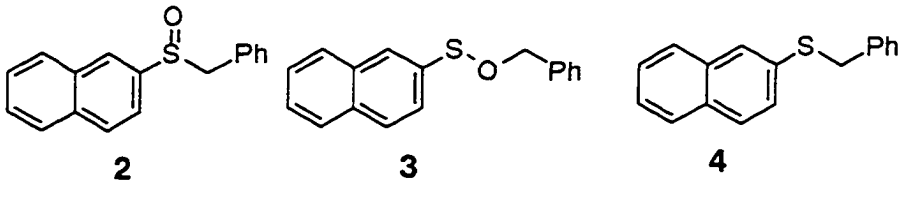
Ar = C_6H_5, *p*-tolyl

R = CH_3, *t*-Butyl, $Ph(CH_2)_n$, $PhCH_2CH(CH_3)$, $Ph(CH_2)_nC(CH_3)_2$, Ph
(n = 1, 2, 3)

Results and Discussion

Photophysical properties

Figure 1 shows the UV absorption spectra of benzyl 2-naphthyl sulfoxide (**2**), sulfenate (**3**) and di-2-naphthyl disulfide (**5**). Compared to benzyl phenyl sulfoxide, 2-naphthyl benzyl sulfoxide shows a red shift in the absorption to above 300 nm. As with the previous case,[1] the corresponding sulfenic ester and disulfide have high absorptions in a higher wavelength region, and competitive secondary photolysis is to be expected.



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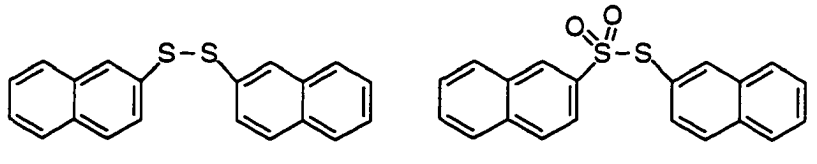

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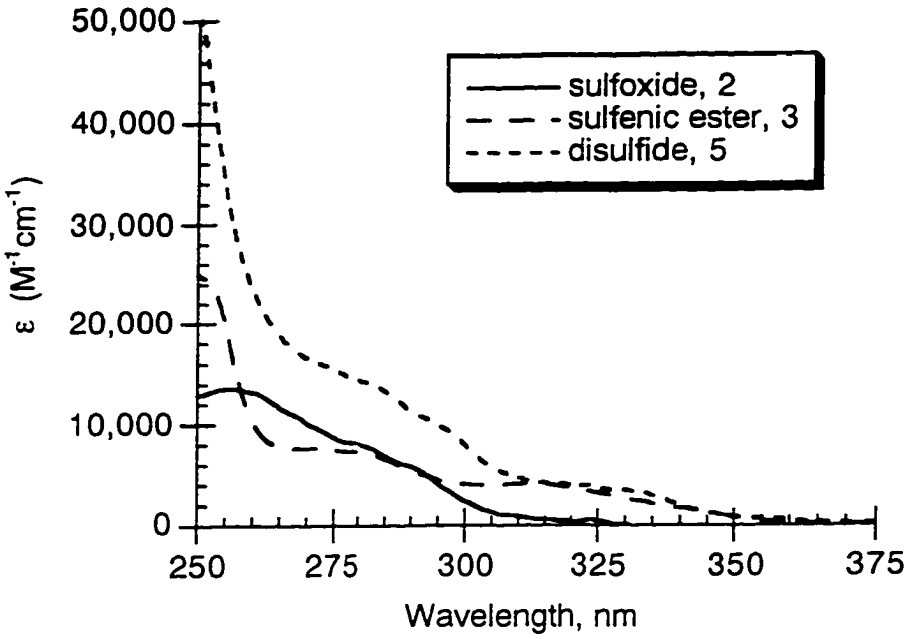


Figure 1. UV absorption spectra of **2**, **3**, and **4** in acetonitrile.

The photophysical properties of several aromatic sulfoxides have been studied in our laboratory.[2] It was observed that the alkylsulfinyl groups can reduce the fluorescence lifetime and fluorescence quantum yield of the arenes. Phosphorescence spectra are similarly weak, 2-naphthyl benzyl sulfoxide (**2**) is no exception. The photoluminescence of **2** at 77 K was investigated (Figure 2). This compound shows florescence at 310–410 nm (singlet energy E_S = 89.7 kcal/mol with a quantum yield Φ_F = 0.009±0.002) and phosphorescence at 450–630 nm (triplet energy E_T = 61.1 kcal/mol with a quantum yield Φ_P = 0.050±0.005). The intersection between the normalized fluorescence and excitation spectra was estimated as the singlet energy, and the first band from the high energy end of the phosphorescence spectra was used to measure the triplet energy.

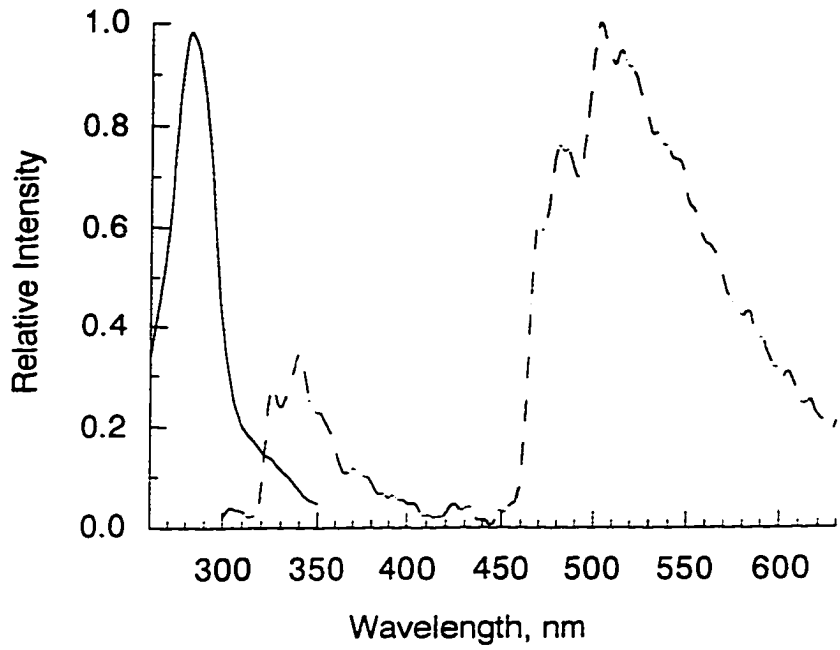
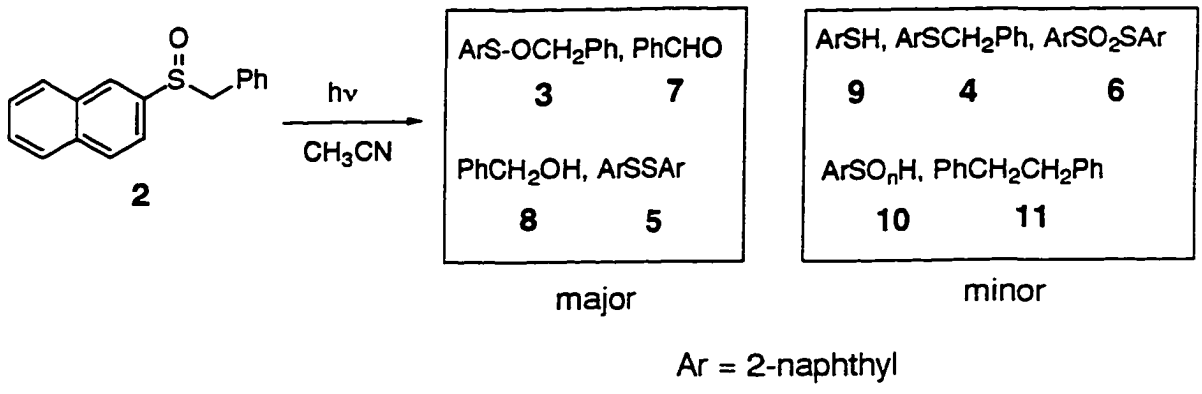


Figure 2. The absorption and emission spectra of **2** at 77 K.

Photolysis products

α-Cleavage of sulfoxides is the most important primary photochemical process in both solution and solid state. The formation of the sulfinyl-alkyl biradical depends greatly upon the structure of the sulfoxide and the photolysis conditions.[3] Usually, the photolysis of sulfoxides is very sensitive to secondary photolysis. and gives complicated mixtures of products if carried out to completion. The benzyl aryl sulfoxide gave a relatively less complicated product mixture than other aryl alkyl sulfoxides because of the dominant high efficiency of α-cleavage and absence of β-hydrogens.

The product analyses of Figures 3 and 4 show the dominant α-cleavage of the S-benzyl bond. In no cases were naphthalene or 2-naphthol detected, which rules out the possibility of the existence or significance of aryl-S bond cleavage, which is consistent with our research on other benzyl aryl sulfoxides.



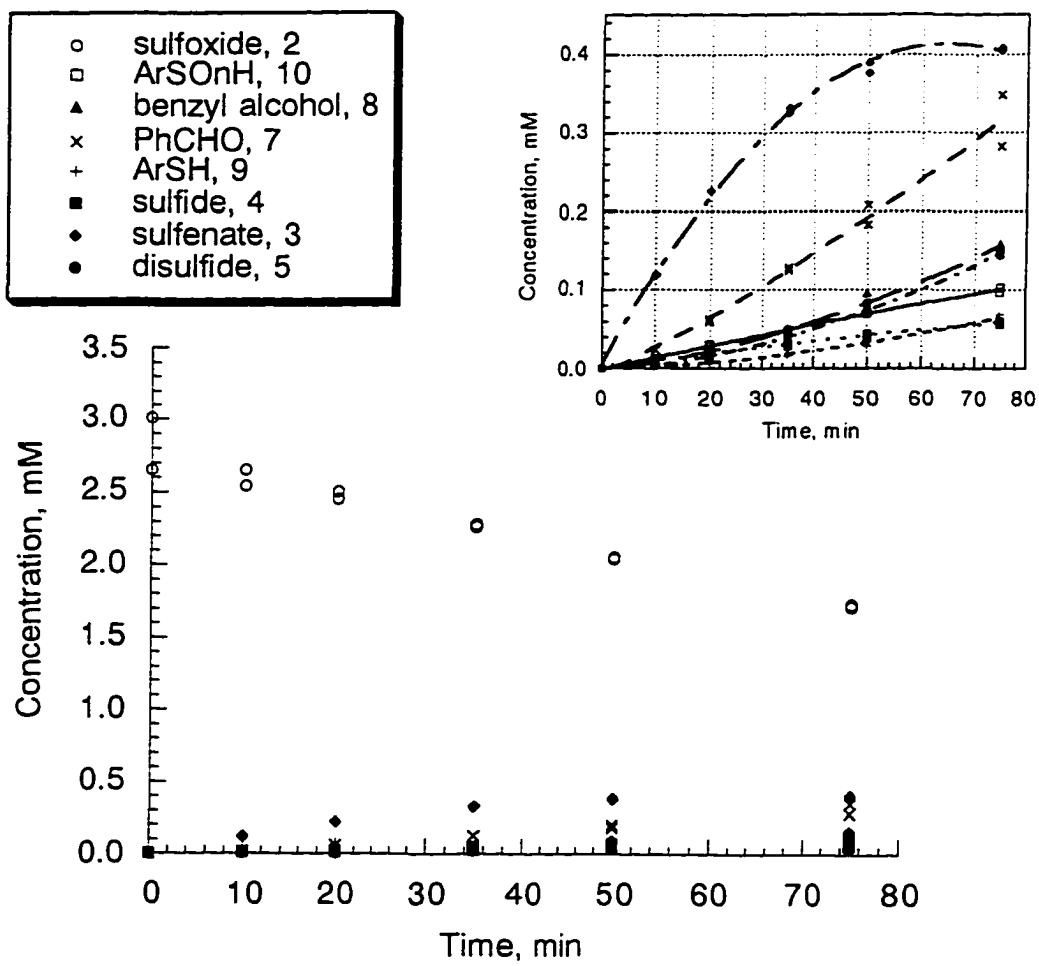


Figure 3. Photolysis of sulfoxide **2** in acetonitrile at 267 nm. Insert: blowup of the photolysis products.

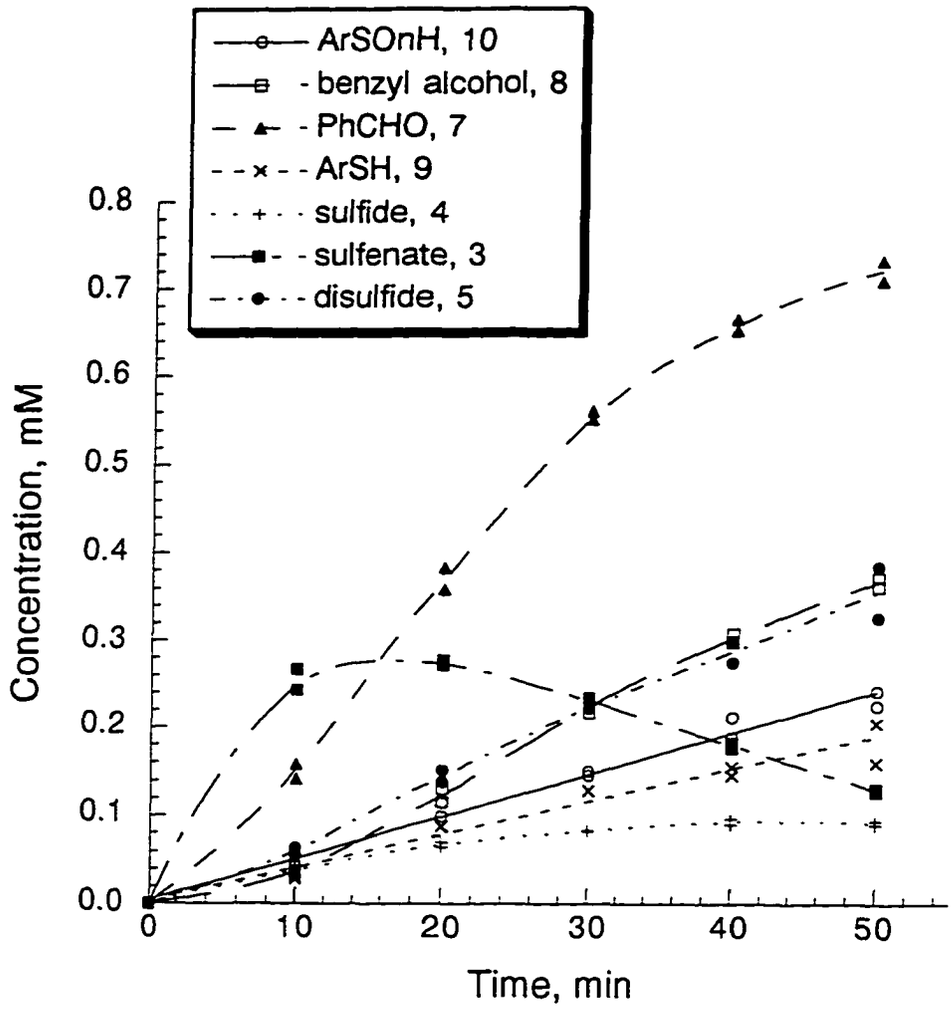


Figure 4. Photolysis of **2** in acetonitrile at 294 nm.

Analysis of Figure 3 shows that benzaldehyde (**7**), benzyl alcohol (**8**), 2-naphthalenethiol (**9**) and disulfide (**5**) all have two-photon formation profiles, which are in accordance with our mechanism assumption in the study of benzyl phenyl sulfoxide.[1] At the same time, both sulfenic ester **2** (at low conversion) and benzyl naphthyl sulfide **4** show linear one photon profiles.

From the analyses of products observed in acetonitrile solvent, we can assume that the excited state of **2** is a singlet. Also, the sensitizer effect of acetone from Table 1 was very similar to that observed in the photolysis of benzyl phenyl sulfoxide,[1] with a typical dramatic

increase of both bibenzyl and aryl thiosulfonate. This is not unexpected when we compare the triplet energy of acetone (78 kcal/mol) and **2** (61 kcal/mol). Noticeably, we still observed some sulfenic ester even in the benzyl 2-naphthyl sulfoxide sensitized photolysis (Table 1). This is consistent with our previous assumption[1] that sulfenic ester can be formed under both direct and sensitized conditions, but the benzyl benzenesulfenate was not observed due to

Table 1. Relative yield of photolysis products of **2** under different conditions.*

	acetonitrile	acetonitrile	acetone	solid
Product	**267 nm**	**294 nm**	**267 nm**	**300 nm**
3	60	41	15	1
4	5	6		6
5	4	10	3	20
6			24	
7	16	25	8	39
8	5	6	5	5
9	2	5	4	12
10	8	7	10	2
11			31	

* All conversions ≤ 15%.

selective sensitization. Such selective sensitization will not be observed in the photolysis of 2 because the triplet energy of **2** and corresponding sulfenic ester are both below that of acetone.

Compared to our previous study on the photolysis of other aryl alkyl sulfoxides, the photolysis of sulfoxide **2** gave a better balance between the arylsulfur part and benzyl part (within 10%) with the exception of the photolysis in the solid state where significantly less benzyl part was found. Part of the reason for the better balance have is because we have taken into account of 2-naphthalenesulfinic acid (**10a**) and 2-naphthalenesulfonic acid (**10b**). Their ratio was not determined because of their inefficient separation on HPLC. The presence of both acids can be detected by the diode array detector of HPLC, although their formation mechanism is still not clear.

Photodeoxygenation

From the photolysis of sulfoxide **2** we observed the near linear formation of sulfide **4** (Figure 5). The deoxygenation reaction was also observed in the photolysis of aryl primary alkyl sulfoxides in both solution and the solid state.[1] One possibility for sulfide formation is the combination of thiyl radical (from secondary photolysis of **3**) and benzyl radical (from α-cleavage of **2**). This is reasonable for the photolysis in solution, but should be quite difficult in solid phase photolysis where the radicals are less mobile. These observations are consistent that in the excited state there may exist a one-photon deoxygenation process which competes with α-cleavage process, although this process is less important (less than 10% from product ratio) compared to α-cleavage process. It has been estimated that the α-cleavage of DMSO into methanesulfinyl and methyl radicals has a dissociation energy D_{C-S} = 52.6 kcal/mol,[4] whereas S=O bond energies are typically 87–90 kcal/mol.[5] The formation of sulfide was also observed in the photochemical study of some other naphthenyl sulfoxides by Still and coworkers.[6] The disproportionation mechanism (forming one molecule of sulfide and one molecule of sulfone) was ruled out because no sulfone was found.

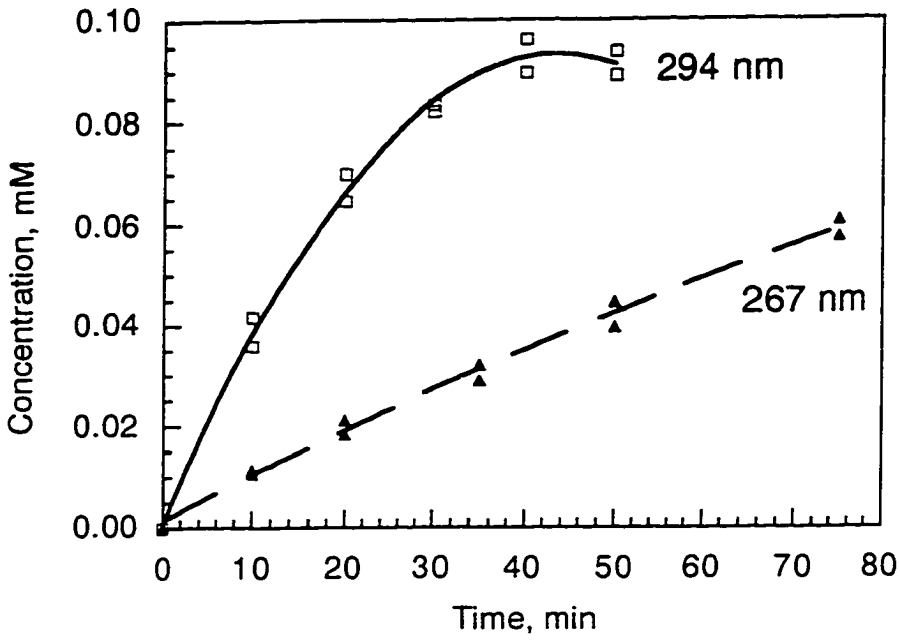


Figure 5. The production of sulfide **4** from the photolysis of **2** in acetonitrile at different wavelength. Note the near linearity in the low conversion region. The slope difference is not related to the production quantum yields because of the different light intensity at different wavelengths.

The mechanism for the photodeoxygenation of sulfoxides is still unsettled.[4,7-9] Recently, it was found that the photolysis of dibenzothiophene sulfoxide produces dibenzothiophene in low quantum yield, but very high chemical yield.[10,11] Mixing sulfoxides photolysis and concentration experiments ruled out the dimer mechanism. The proposed mechanism based on sulfinyl radical O-atom transfer was ruled out on energetic basis. The possibility of an intermolecular hydrogen abstraction mechanism was also very small because of the insensitivity to the hydrogen donor strength of the solvents. A unimolecular S-O bond cleavage mechanism was proposed.

Photolysis quantum yields

Because of the relatively low solubility in most organic solvent, the photolysis of naphthenyl benzyl sulfoxide were studied in acetonitrile and acetone. Generally, its photolysis is very similar to phenyl benzyl sulfoxide but with somewhat lower quantum yields (Table 2).

Table 2. Quantum yields for the disappearance of **2** using different solvents and irradiation wavelengths.

solvent	267 nm	294 nm
acetonitrile	0.12	0.16
acetone	0.19	0.22

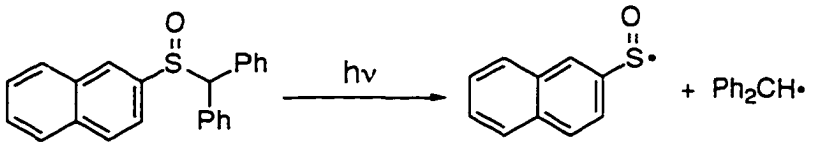
In order to better understand the excited state of sulfoxide **2**, we studied the photolysis in the presence of the isoprene triplet quencher. Benzyl naphthenyl sulfoxide was irradiated in the presence of different concentrations of isoprene in acetonitrile at 300 nm using a Rayonet. Although the presence of isoprene quenched the disappearance of sulfoxide, the results are complex. The non-linear relationship between quantum yield and quencher concentration may suggest the possible existence of other "reverse quenching" processes (such as the reaction between isoprene and arylsulfinyl-benzyl radical pair or the formation of sulfoxide-isoprene exciplex).

Laser flash photolysis

The α-cleavage of sulfoxides gives sulfinyl and alkyl radical pairs. The photochemical properties of alkyl radicals have been well documented.[12,13] Meanwhile, there is very limited knowledge about sulfinyl radicals,[12,13] although some arylsulfinyl radicals have been observed by EPR[14] and CIDNP[9]. The chemistry of thermally generated sulfinyl radicals has also been investigated.[12] Unlike the benzoyl radical, the phenylsulfinyl

radical is a *p*-delocalized species and appears to be relatively stable. No adducts or polymerization are observed when they are generated in the presence of alkenes. It also appears that they add to alkenes reversibly.[15,16] This is important, because it may limit the possibility of using sulfoxides as photoinitiators in polymerization.

Recently we studied the formation and photochemical properties of phenylsulfinyl radical and determined the rate constants for its reaction with free stable radicals in solution.[17] As in the study of benzyl phenyl sulfoxide, the absorption of the benzyl radical is observed with two strong maxima at 258 and 316 nm which interferes with sulfinyl radical absorption. In order to obtain the absorption spectra of 2-naphthylsulfinyl radical **13**, we synthesized diphenylmethyl 2-naphthyl sulfoxide (**12**). The diphenylmethyl radical **14** has been well characterized,[18-21] and has maxima at 331 and 318 (shoulder) with extinction coefficients of 4.4 x 10^4 M^{-1} cm^{-1} and 3.1 x 10^4 M^{-1} cm^{-1} respectively.



12 **13** **14**

The experiment was carried out in oxygen saturated solution. The Ph_2CH• radical reacts very efficiently with oxygen and its life time should be ~70 ns. The absorption spectra of the transient with maximum at 310 nm recorded 100 ns after laser pulse refers to the absorption of the 2-naphthylsulfinyl radical **13** (Figure 6). The extinction coefficient of radical **13** at 310 nm can be estimated as 1.3 x 10^4 M^{-1} cm^{-1}. The decay of this radical at 310 nm is very well fit to the second order kinetics with the decay rate constant of recombination $2k_r$ = 3.6 x 10^9 M^{-1} s^{-1} and 5.1 x 10^9 M^{-1} s^{-1} in CH_3CN and hexane respectively. These rate constants are the same in air and oxygen saturated solutions. Photolysis at various temperatures gives a rough estimate for the activation energy of the radical recombination reaction in acetonitrile E_a = 0.2 ± 0.1 kcal/mol. The reaction of **13** with nitroxides (e.g.

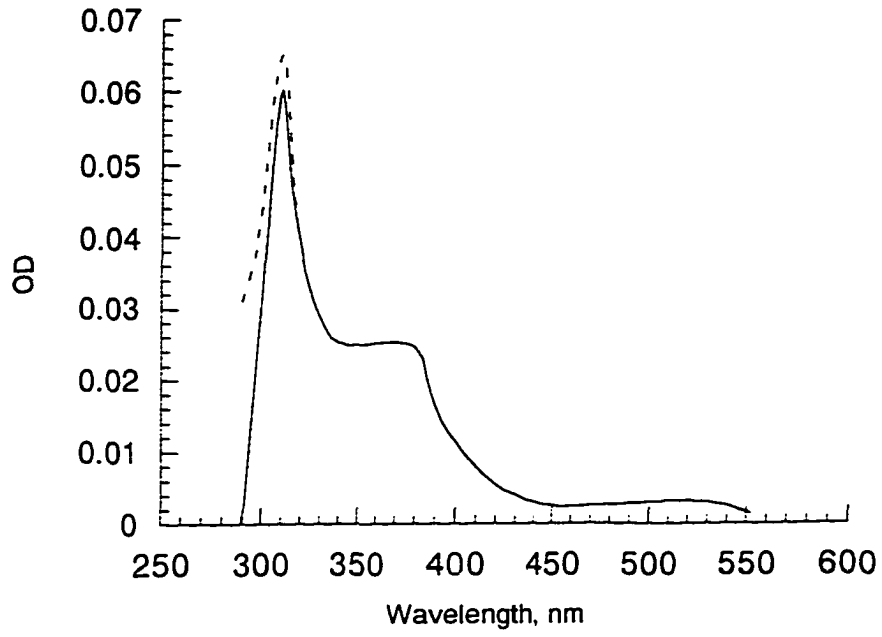


Figure 6. Differential absorption spectrum of the 2-naphthylsulfinyl radical (**13**) upon excitation of sulfoxide **12** (2.3 x 10^{-5} M) in air-saturated acetonitrile 200 ns after laser pulse (solid line). Absorption spectrum of **13** is corrected for the ground state bleaching of **12** (dashed line).

TEMPO and DTBN) follows pseudo-first order kinetics and depends linearly on the concentration of the nitroxides.

Summary

The data presented in this paper strongly support that the photolysis of benzyl 2-naphthenyl sulfoxides proceeds largely through the mechanism outlined in Figure 7, which is in good agreement with the study of other benzyl aryl sulfoxides. The primary process is cleavage of the S–C bond in an excited singlet state with the efficient formation of a sulfenic ester intermediate. The secondary photolysis of sulfenic ester gave other observed products

and its efficiency related to the irradiation wavelength . The sulfoxide can be efficiently sensitized by acetone which gave mostly triplet radical pair chemistry which shows higher quantum yields than singlet chemistry. A possible unimolecular deoxygenation reaction accounts for the formation of sulfide product.

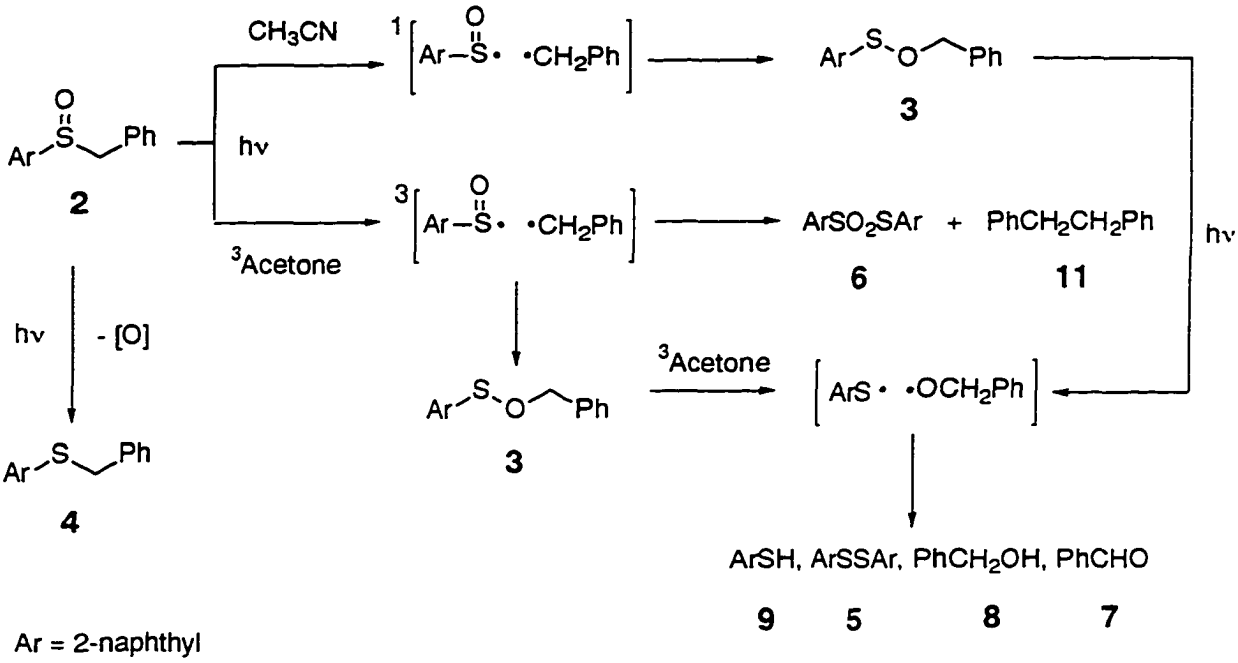


Figure 7. Proposed photolysis reaction mechanism of **2**.

Experimental Section

General methods. Except as noted, HPLC grade solvents were used as received for all photolyses. All melting points are 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 on a HP 5890 Series II gas chromatograph equipped with an FID detector and a 10 m HP-1 column. HPLC data were collected on a HP 1050 liquid chromatograph with a diode array detector. An ODS Hypersil reverse phase

column (5μm, 200 x 2.1mm) 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%. The luminescence and quantum yield were recorded with an Edinburgh Instruments FL900 spectrometer. A suprasil liquid nitrogen immersion dewar was used to hold the sample in quartz NMR tube at 77 K. To measure the phosphorescence spectra and quantum yield, sulfoxide **2** was dissolved in a 1:1 mixture of ethanol and methanol (which forms a glass at 77 K). Benzophenone was the standard for measuring quantum yields. The optical density of the sample solution and benzophenone was maintained about 0.1 and 0.04 respectively at 270 nm.

Synthesis of compounds.

Benzyl 2-naphthenyl sulfide (4). This compound was synthesized from 2-naphthalenethiol and benzyl bromide in THF using a method described before.[3] The crude product was purified by recrystallization from methylene chloride: yield 95%; mp 87–88 °C (lit.[22] mp 88 °C); ^{1}H NMR ($CDCl_3$) δ 4.22 (s, 2 H), 7.20–7.95 (m, 12 H). ^{13}C NMR ($CDCl_3$) δ 38.8, 125.6, 125.7, 126.3, 127.1, 127.33 127.5, 127.6 128.2 128.4 128.7, 131.7, 133.6, 133.8, 137.2.

Benzyl 2-naphthenyl sulfoxide (2). This sulfoxide was synthesized by oxidizing benzyl 2-naphthyl sulfide (**1**) using 4-8 equivalents of H_2O_2 according to a literature method.[23] Acetone was used as the solvent because of the low solubility of sulfide **4** in methanol. More acetone may be used to make sure a clear solution is obtained at the beginning of the oxidation. This reaction may take several days and was monitored by TLC. Sulfoxide **2** precipitated from the solution. The crude product was further purified by recrystallization from methylene chloride: mp 189-190 °C; ^{1}H NMR ($CDCl_3$) δ 4.08 (d, J = 12.6 Hz, 2 H), 4.17 (d, J = 12.6 Hz, 2 H), 6.98–7.02 (m, 2 H), 7.19–7.30 (m, 3 H), 7.41 (dd, J = 8.7, 1.8 Hz, 1 H), 7.52-7.62 (m, 2 H), 7.80–7.92 (m, 4 H).

Diphenylmethyl 2-naphthyl sulfoxide (12). This sulfoxide was synthesized by oxidizing the corresponding sulfide as described before,[17] and was purified by recrystallization from methylene chloride to a light yellow solid. ^{1}H NMR ($CDCl_3$) δ 4.92 (s, 1 H), 7.24–7.39 (m, 11 H), 7.19–7.30 (m, 3 H), 7.47–7.57 (m, 2 H), 7.72–7.85 (m, 4 H). ^{13}C NMR ($CDCl_3$) δ 77.7, 125.9, 127.1, 127.7, 128.0, 128.3, 128.5 (2 overlapped peaks), 128.6, 128.8, 129.4, 129.7, 132.6, 134.0, 134.5, 135.4.

Di-2-naphthyl disulfide (5). This disulfide was prepared in about quantitative yield following the literature procedure:[24] I_2 (0.5 mmol) dissolved in 25 ml ether was added to the 25 ml ether solution of 2-naphthalenethiol (1 mmol) and Et_3N (1 mol) at ice bath. The reaction was allowed to run at room temperature over night. The reaction mixture was transferred to a separation funnel, add water, ether layer was separated and washed three times with sodium bicarbonate solution. The crude product was recrystallized from methylene chloride: mp 139–140 °C (lit.[25] mp 136–138 °C); ^{1}H NMR ($CDCl_3$) δ 7.44–7.50 (m, 4 H), 7.65 (dd, J = 1.6, 8.4 Hz, 2 H), 7.70–7.80 (m, 6 H), 7.98 (d, J = 1.6 Hz, 2 H).

2-Naphthalenesulfinic acid (10). This compound was synthesized by the reduction of 2-naphthalenesulfonyl chloride with sodium sulfite according to literature procedure,[26] and was purified by recrystallization from hot water: yield 80%; mp 94–96 °C (dec.) (lit.[27] mp 95–100 °C (dec.)); ^{1}H NMR ($CDCl_3$) δ 7.55–7.64 (m, 4 H), 7.76 (dd, J = 8.4, 1.5 Hz, 2 H), 7.89–8.00 (m, 6 H), 8.24 (s, broad, 2 H). MS (CI, NH_3): 210 (70, MNH_4^+), 193 (18, MH^+), 175 (100, ArSO).

2-Naphthyl 2-naphthalenethiosulfonate (6). This compound was synthesized from the oxidation of the disulfide by hydrogen peroxide in acetic acid according to a literature procedure.[28] Recrystallization from methylene chloride gave a light yellow solid. mp 104–105 °C (lit.[29] mp 106–107 °C); MS (CI, NH_3): 368 (100, MNH_4^+), 350 (12, M^+).

Benzyl 2-naphthalenesulfenate (3). This compound was synthesized by the reaction of 2-naphthylsulfenyl chloride and benzyl alcohol in anhydrous methylene chloride

according to a literature procedure.[30] After workup, the crude product was recrystalized from CH_2Cl_2/hexane. HPLC analysis showed approximately 90% purity with the disulfide as major impurity. Distillation and chromatographic methods cause further decomposition. ^1H NMR ($CDCl_3$) δ 4.83 (s, 2 H), 7.30–7.40 (m, 5 H), 7.44–7.55 (m, 3 H), 7.75–7.90 (m, 4 H). ^{13}C NMR ($CDCl_3$) δ 38.77, 122.8 (2 overlapped peaks), 126.1, 126.8, 127.6, 127.9, 128.5 (3 overlapped peaks), 128.8, 132.3, 133.5, 137.0, 137.6. This compound is very thermally labile, under mass spectral analysis condition, it shows peaks derived from **4** and **5** besides ArS and ArSO fragments. 2-Naphthylsulfenyl chloride was synthesized by reaction of 2-naphthalenethiol and sulfonyl chloride using CH_2Cl_2/hexane (1/1) as solvent following a literature procedure.[31] After vacuum distillation of the solvent, the orange yellow oily product was used without further purification.

Product identifications. Product identification was based on comparison to genuine samples in chromatographic behavior. HPLC-derived UV spectra were obtained and compared. Once products were established, comparison of retention times for experimental and genuine samples were reverified for any change of chromatographic conditions.

Photolyses. Unless otherwise indicated, photolyses were carried out using a 150 W Xe lamp and monochrometer setup from Photon Technologies, Inc. The linear dispersion of the monochrometer 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 UV cells, which are positioned exactly at the exit of the monochromator so that the maximum amount of the exiting light hits the sample. All solution photolyses were carried out with magnetic stirring and after Ar flushing to remove O_2. Sometimes, photolyses were carried out using an RMR-500 "mini-Rayonet" from Southern New England Ultraviolets. 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.

Laser flash photolysis. All experiments were carried out using a nanosecond laser photolysis technique as described before.[17] The solution were irradiated with a 266 nm laser pulse, 5 ns, 5–20 mJ of Nd:YAG laser. The optical density of the solutions were ~ 0.3 at 266 nm. Experiments were usually carried out at 23 °C. The thermodynamic parameters of reactions were measured in the range of 0–60 °C . The solutions were flushed with argon or oxygen for 20 minutes when it is necessary. The accuracy of the quantum yield, the extinction coefficient of 2-naphthylsulfinyl radical and the rate constants are all within ±15%.

Solid state photolysis. Approximately 5–10 mg of sulfoxide was dissolved in methylene chloride. This solution was used to coat the inside of a Fisher Borosilicate glass tube with the solid material and blanketed with Ar under a septum. This tube was positioned inside the Rayonet described above and photolyzed with appropriate wavelength bulbs. The tubes were kept at room temperature by a cooling fan. After photolysis, the solid was dissolved in acetonitrile and analyzed by HPLC.

Quantum yields. Quantum yields were determined using a PTI lamp. The actinometer was azoxybenzene.[32] The quantum yield of 0.018 at 267 nm and 0.021 at 294 nm were used respectively. Quantification of sulfoxide photolysis products was done by HPLC. 1-Phenylundecane was used as internal standard. Sample and actinometer cells were sequentially irradiated and the latter was 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 20%.

Acknowledgment. We gratefully acknowledge financial support from the NSF (CHE 94-12964), the Petroleum Research Foundation, and the Research Corporation. Y.G. thanks the Dow Chemical Fellowship and Nelson Chemistry Scholarship at Iowa State University. The authors also express their gratitude to Dr. Alexander P. Darmanyan for the laser flash

photolysis experiment and Mr. Woojae Lee for help in measuring the emission spectra and excited state energy.

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CHAPTER IV

PHOTOLYSIS OF ALKYL ARYL SULFOXIDES: α-CLEAVAGE, HYDROGEN ABSTRACTION, AND RACEMIZATION[1]

A paper, a portion of which was published in the *Journal of Organic Chemistry*

Yushen Guo and William S. Jenks

Abstract: 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 alkenes and arenesulfenic acid, and the formation of typical radical escape products. The quantum yield for conversion depends on the structure or the reactivity of the alkyl radical, with the following order: benzyl > tertiary alkyl > secondary alkyl > primary alkyl > (di-)aryl. The high racemization efficiency of some aryl primary-alkyl sulfoxides suggests the possible existence of another non-radical pathway for the photoracemization process. Product analysis does not support any hydrogen abstraction pathways. The direct observation and characterization of arylsulfinyl radicals from laser flash photolysis strongly supports the α-cleavage primary process.

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] Though 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, especially in the simple acyclic sulfoxide systems.

Most of the previous sulfoxide substrates have been cyclic or carbonyl-containing structures and we felt it desirable to use simple acyclic test cases to insure that the chemistry was completely consistent with C-S homolysis. Recently we reported the photochemistry of aryl benzyl sulfoxides 1.[9] 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 (1,2-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 included sulfoxide α-cleavage, is illustrated in Figure 1.

It is noteworthy that, α-cleavage has been invoked for much less favorable structure types than 1. Figure 2 illustrates a few examples in which less than ideal radicals would be

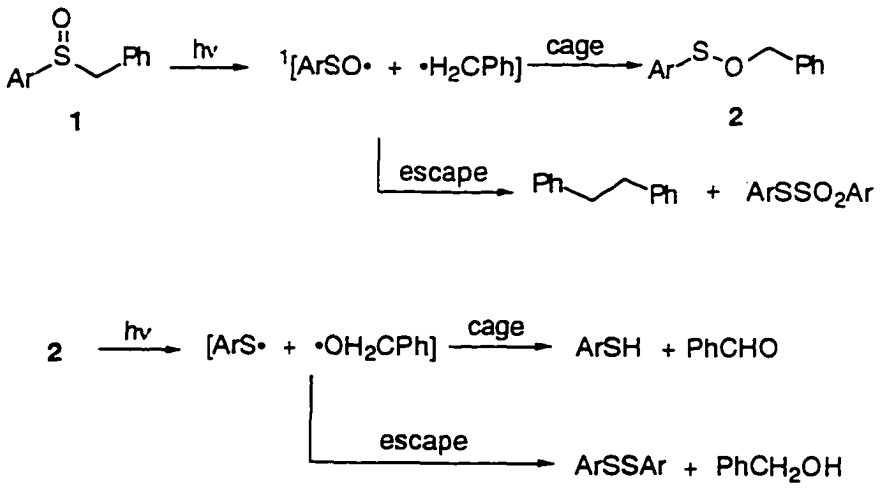


Figure 1. Proposed photolysis mechanism of aryl benzyl sulfoxides.

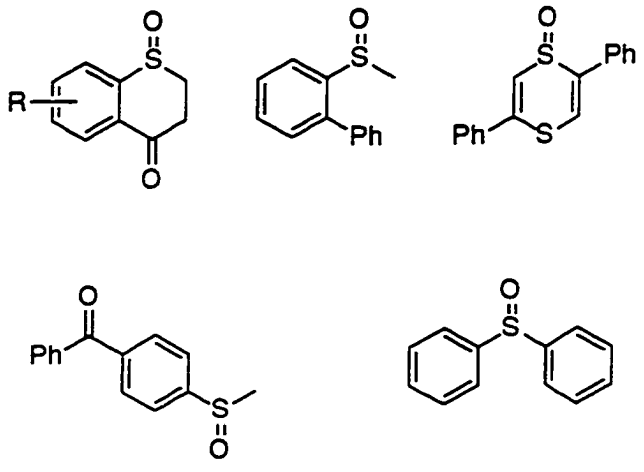


Figure 2. Examples of α-cleavage related to unfavorable radicals.

produced on C-S homolysis.[2,8-18] If correct, these examples point out that the sulfoxide is significantly more susceptible to photochemical α-cleavage than its carbonyl analog.

A series of alkyl aryl sulfoxides with structural variations (Figure 3) were prepared. We studied their photolysis as part of an attempt to clarify the photochemistry of aromatic sulfoxides in general, and also to try to answer some related questions. We report an examination of the effect of molecular structure on the proclivity of the compound for α-cleavage and the selectivity of that cleavage for either C-S bond. In each case, one of the substituents is either a phenyl or *p*-tolyl group. The other substituents are either a primary, secondary, tertiary, benzyl, or aryl group, but is remotely labeled with a phenyl group in the first three cases for ease of detection.

Among the issues addressed is the quantum efficiency for the photo reaction as a function of the 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.

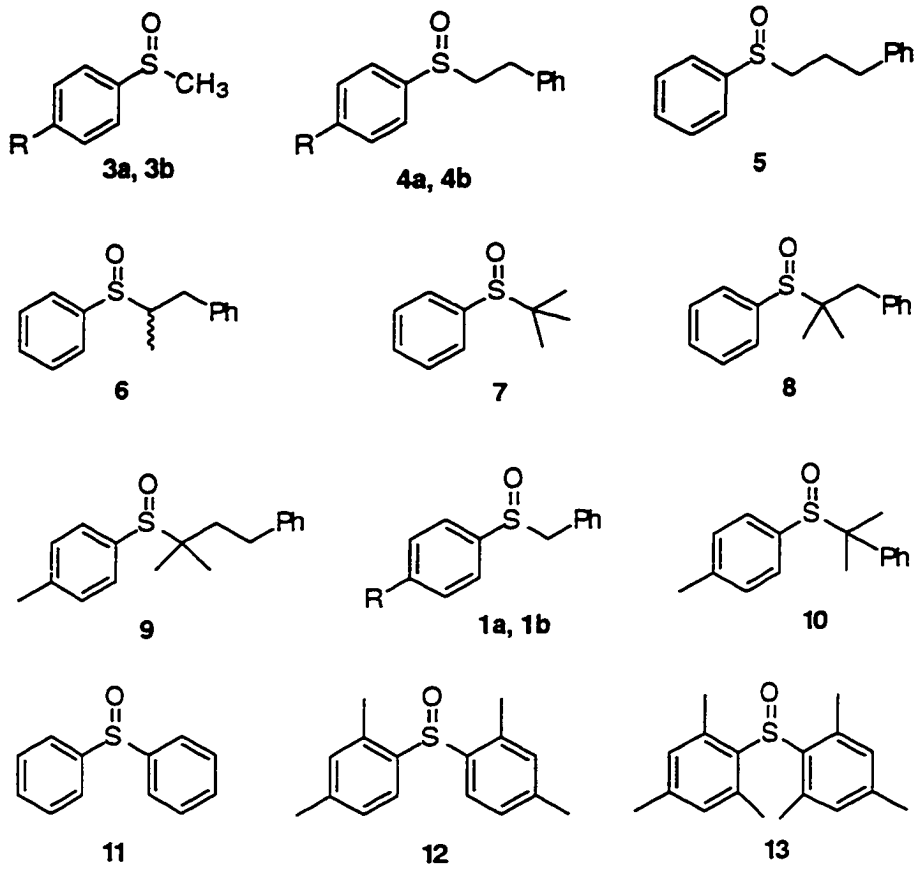


Figure 3. Structures of the sulfoxides under investigation.

Two other significant issues are also addressed. First is the matter of hydrogen abstraction by sulfinyl groups. 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 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 have been 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 have found two primary sulfoxides whose quantum yield for stereomutation is more than an 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 this study, all of which have a phenyl or *p*-tolyl substituent, are illustrated in Figure 3. As to the second 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 by compounds **11–13**.

Synthesis of sulfoxides

Primary alkyl aryl sulfoxides and benzyl aryl sulfoxides were synthesized by oxidation of correspondent sulfide by hydrogen peroxide in methanol or acetone. The sulfides were prepared by direct nucleophilic substitution of the appropriate alkyl halides or alkyl tosylate by the arenethiols (Figure 4).

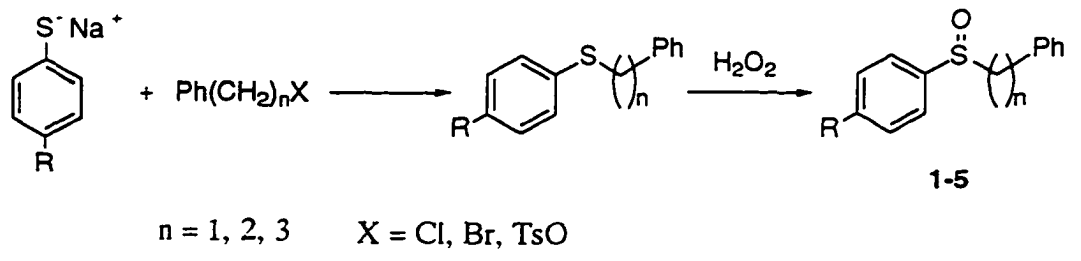


Figure 4. Synthesis of sulfoxides **1-5**.

Sulfoxides **7–9**, and **10** cannot be synthesized by the procedures described in Figure 4, due to E2 elimination which gives alkenes as the major products. We therefore used a modified literature method[20] to synthesize the sulfides from the arenethiol and alcohol (or alkene) under strong acidic conditions (Figure 5). The sulfide was oxidized by the hydrogen peroxide-urea complex, which have proven very effective for the oxidation of structurally hindered sulfoxides in good overall yields.[21] Optically pure **5** was obtained by the Andersen reaction[22] of menthyl benzenesulfinate with the corresponding organometallic regent (Figure 6), and was purified by repeated recrystallizations. Sulfoxide **6** was prepared the same way as a mixture of two diastereomers.

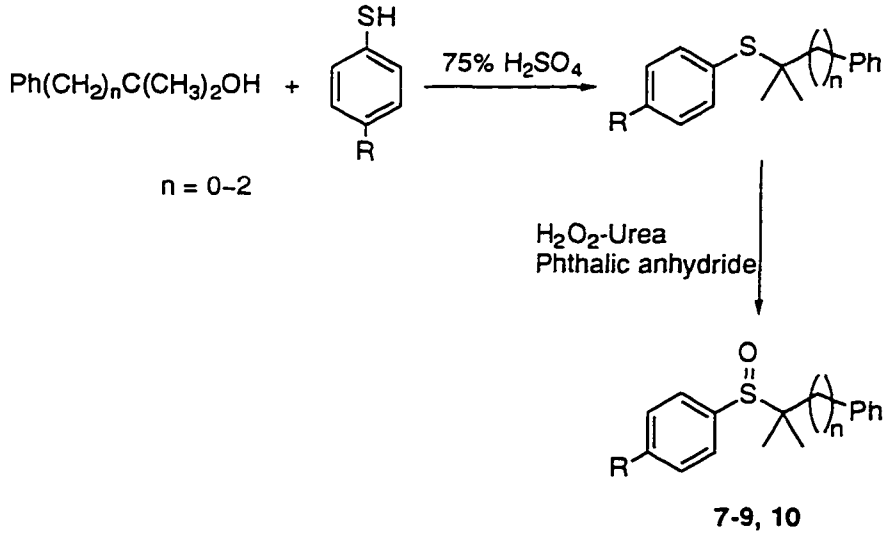


Figure 5. *Synthesis of sulfoxides* **7-9, 10.**

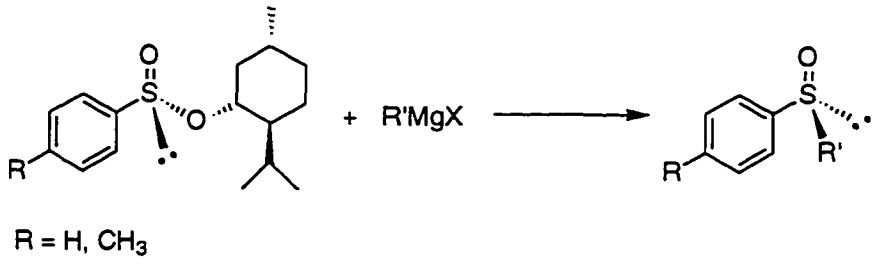


Figure 6. Andersen reaction for the synthesis of chiral sulfoxides.

Spectroscopic properties

In solution, all alkyl aryl sulfoxides possess a strong (ε = 4000–6000), and relatively broad absorption band maximizing in the 230–260 nm region. This band undergoes a red-shift with increasing alkyl substitution at the α-position. The ultraviolet absorption of several sulfoxides were measured in 2-propanol. These sulfoxides show a small, but regular increase in absorption maximum (~ 6 nm) and extinction coefficient (300–600) with increasing alkyl substitution in the α-position. The phenyl group has a bigger substitution effect, especially at the α-position (**1a**).

Florescence and phosphorescence of sulfoxides are rarely observed in solution at room temperature.[23] It is difficult to assign accurate excitation energies to the S_1 and T_1 states. Approximate values can be expected for the S_1 (90–100 kcal/mol) and T_1 (75–80 kcal/mol) states from some studied sulfoxides.[23]

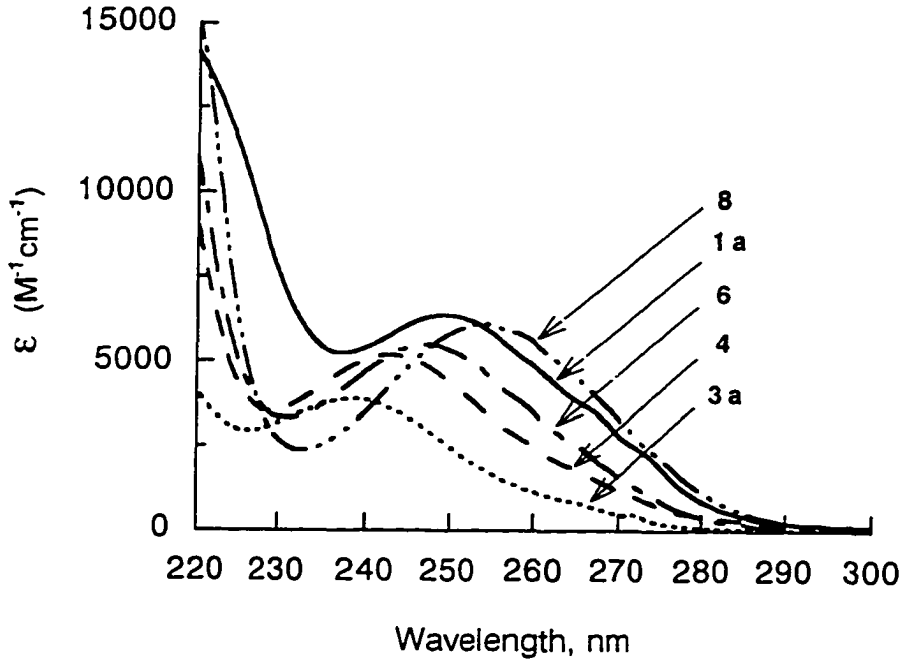


Figure 7. UV absorption spectra of some sulfoxides in 2-propanol.

Photolysis products

Photolyses of the sulfoxides in Figure 3 until completely consumed create 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 caused by the thermal chemistry of the sulfenic acids and esters that are produced as primary products.[24] Sulfenic acids condense to thiosulfinic esters, which in turn disproportionate to disulfides and thiosulfonates. Hydrolysis of a thiosulfonate affords sulfinic and sulfonic acids. We also find that photolysis of the arenethiosulfonates provides sulfinic and sulfonic acids, along with disulfide. The relative yields of arylsulfinic and arylsulfonic acids increased when the photolysis solution was not purged with argon. The photo-generation of strong acids may be interesting because there are already some examples where sulfur compounds are used as photo-initiators for acid-catalyzed polymerization.[25,26]

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,[27] 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

Table 1. Photolysis products and yields for photolysis of sulfoxides.

Cmpd	Solvent	Products (% Yield)[a]	Mass Balance Aryl	Mass Balance Alkyl
4a	*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)	f	f
4a	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)	f	f
4a	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

Table 1. (continued)

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), $PhCH_2CH=CMe_2$ (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 at ≤10% conversion. (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. (f) See text.

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.

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 **4a** 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 **4a** 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 7. Minor amounts of the deoxygenation product were observed on acetone-sensitized photolysis of **4a** and **5**.[28] Only benzaldehyde, which is a component of the mixture for **4a** and **6**, and **8**, is unaccounted for using schemes like Figure 7. This will be discussed in more detail in the section on internal hydrogen abstraction.

The solvent effects, reported explicitly for **4a** and **5**, are consistent with those previously reported for **1**.[9] In comparison to 2-methyl-2-propanol, using 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,[29] but this was not thought to be significant for purposes of this experiment. The

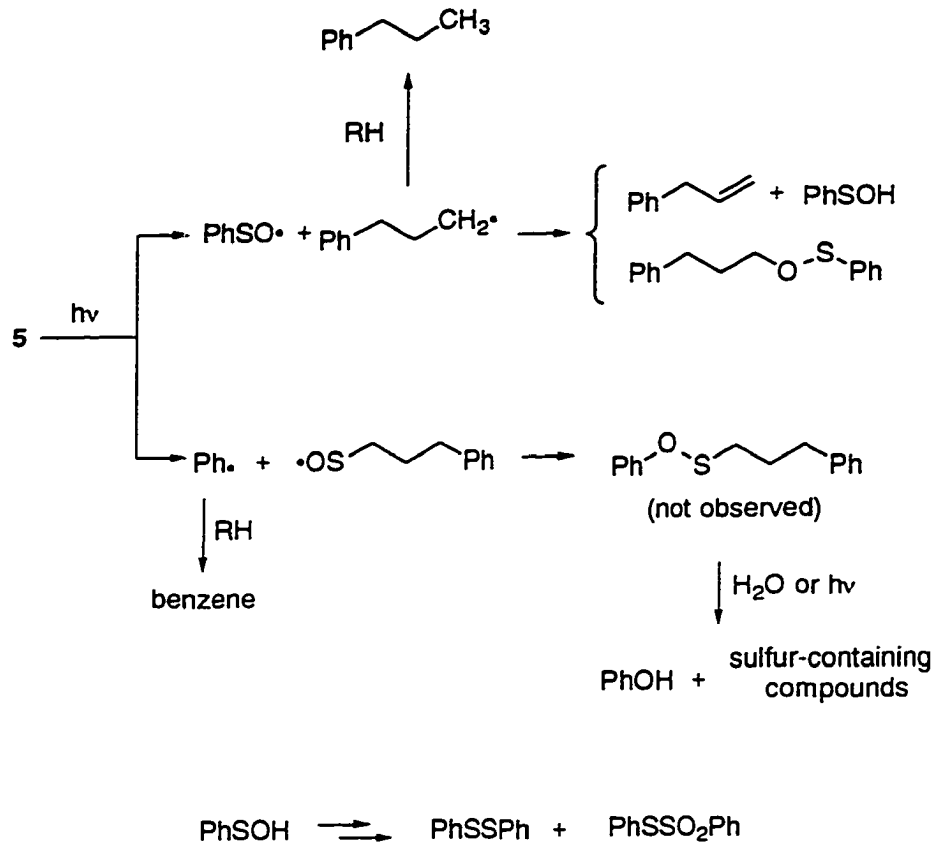


Figure 7. An α-cleavage scheme to account for the products from photolysis of **5**.

triplet energies for these sulfoxides are expected to be on the order of 80 kcal/mol,[23] 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 **4a** 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 **4a**, 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 instability.

Another interesting observation is the relative yields of phenol and 3-phenyl-1-propanol from the photolysis of compound **5** in the solid state. Because the immobility of molecules and radicals in the solid state, we assume this ratio represents the relative α-cleavage activity (Figure 8).

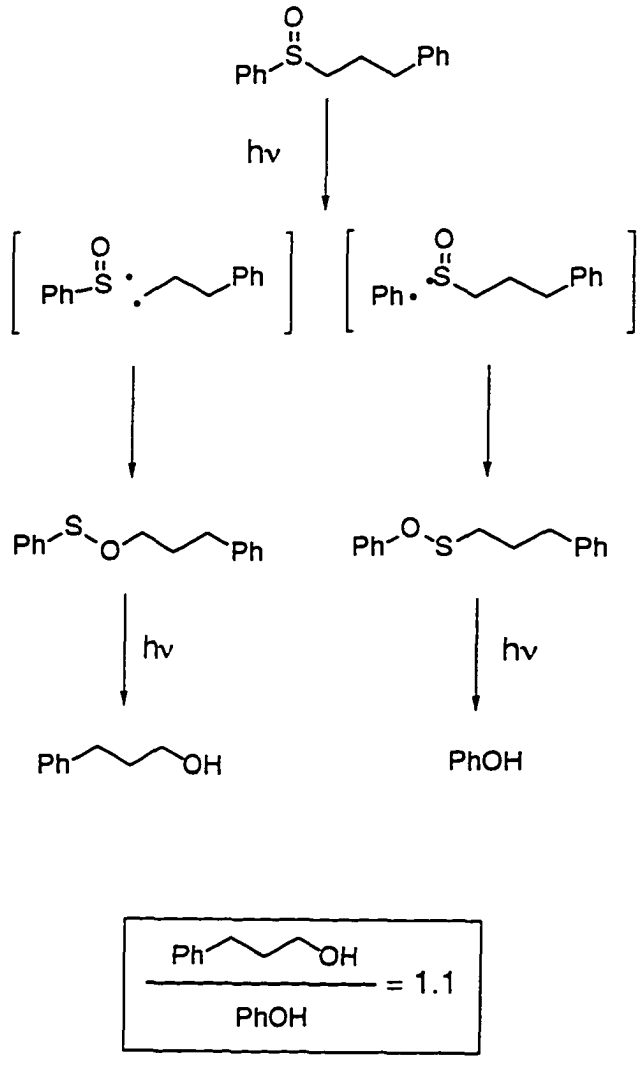


Figure 8. Photolysis of primary alkyl sulfoxide **5** in the solid state.

In order to better understand the aryl-S cleavage in aryl primary alkyl sulfoxides, **4b** was prepared because of the advantage of easier product identification by HPLC. It has a similar quantum yield to that of **4a** in *tert*-butyl alcohol. Product analysis identified the presence of toluene and 4-methyl phenol (ratio 1 : 1.4) which apparently came from the aryl-S cleavage.

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 nearly completely restored if the alkyl group is secondary, tertiary, or benzyl.

Photolysis of diphenyl sulfoxide has been studied by several authors under different conditions.[12,30,31] Biphenyl was one of the major products from its photolysis in benzene, which may come from the reaction between phenyl radical and benzene. In order to compare diphenyl sulfoxide with other alkyl aryl sulfoxide systems, we studied the photolysis of diphenyl sulfoxide in *tert*-butyl alcohol using a 254 nm mercury lamp and quartz tubes and found the following product ratios: benzene : phenol : biphenyl = 1 : 0.4 : 0.1. We also found some other sulfur species consisting of mostly benzenesulfinic acid, benzenesulfonic acid and some diphenyl disulfide. This result supports the observation of arene as a noticeable product in the photolysis of primary alkyl aryl sulfoxides. The arene radicals are very active and can abstract hydrogen from *t*-butanol.

Quantum yields

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.

Table 2. Quantum yields for the disappearance of starting materials in different solvents at 267 nm.[a]

Compound	Quantum yield of disappearance (Φ_{loss})		
	t-BuOH	CH_3CN	Other solvents
3	0.038		0.036[b]
4a	0.037	0.052	0.031[b]
4b	0.036		
5	0.039	0.054	0.031[b]
6	0.072		
7	0.13		
8	0.10	0.15	0.12[c]
9	0.10		0.15[c]
1	0.20	0.28	0.30[b]
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 argon flushed to remove oxygen. Under these conditions, all of the light is absorbed. (b) In 2-propanol. (c) In methylcyclohexane.

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 sulfoxides **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**[32] is somewhat solvent dependent,[28] 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,[33] Benson's estimate for the heat of formation of PhSO•,[34] and experimental heats of formations for phenyl and the various butyl isomers,[33] the resulting bond energies for primary-, secondary-, and tertiary-alkyl phenyl sulfoxides are all in the range of 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 ($E_S \approx$ 90–100 kcal/mol) or triplet ($E_T \approx$ 75–80 kcal/mol) state.

From this data, it can't be explicitly determined whether the trend of the quantum yield 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.[35] 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 non-productive recombination (as opposed to other reactions of the primary radical pair) is very efficient only for the diaryl and aryl primary sulfoxides. As we discussed before,[9] the α-cleavage efficiency is not equal to, but more likely proportional to the quantum yield of the disappearance of the sulfoxides. The results of Table

2 are obviously in accordance with the predictions based on radical stability of the radical pairs.

In the analysis of the photolysis products, we found that the more stable the alkyl radical in the alkyl aryl sulfoxide series, the higher the percentage of the sulfenic ester product observed. This means that the fate of the radical pair from α-cleavage depends not only on outside factors like solvent and temperature, but possible also on the reactivity of the alkyl radicals (or more precisely the sulfinyl alkyl radical pairs). Highly reactive radicals like primary alkyl or phenyl radicals tend to react more indiscriminately. The stable radicals (like benzyl radical) are less reactive toward other neutral species, like hydrogen abstraction. They are more likely to react with another radical (*i.e.* forming sulfenic ester).

Also, there may exist another possible reason for less sulfenate observation, which is related to the sulfenate-sulfoxide quantum yield difference. Supposing that those sulfenic esters have similar photolysis quantum yields (e.g., 0.69), the quantum yield ratio of sulfenic ester to sulfoxide is about 0.35 (0.69/0.20) in the phenyl benzyl sulfoxide case. While in the phenyl primary alkyl sulfoxide or diphenyl sulfoxide cases, this ratio is 18 (0.69/0.038) and 20 (0.69/0.034) respectively. The larger ratio will make the sulfenic ester intermediate less likely to survive the secondary photolysis. We have observed that in the primary alkyl aryl sulfoxide cases, the corresponding sulfenic ester slope began to decrease after about 5% conversion of the sulfoxides. While in the benzyl phenyl sulfoxide case, this starts at about 25% conversion.

The α-position substitution is also a point of interest. It has been shown that the α-cleavage reactivity of ketones is related to the stability of the radicals produced. Substitution on the α-position by alkyl groups increases the excited state ketone (T_1) toward α-cleavage and thus their overall quantum yields.[36] In the study of ketone photochemistry, it was found that the disproportion/coupling ratio of alkyl radicals increases as the radicals go from primary to tertiary.[37] When this was extended to the α-cleavage of aryl alkyl sulfoxides, things become a little bit of more complicated. Since the coupling of the sulfinyl alkyl radical pair gives both starting sulfoxides and product (sulfenate), it is possible that the disproportion process may

contribute more to the quantum yield difference than the coupling process.

Regioselectivity of alkene products

From Table 1, it can be seen that alkene products are obtained from the photolysis of **4–6**, **8**, and **9**. It is proposed that these compounds are formed from the disproportionation of the initial sulfinyl/alkyl radical pair from α-cleavage (*e.g.*, Figure 7). When only one alkene is possible (**4**, **5**), it is the same as is generated thermally in the electrocyclic elimination (Figure 9).[38-41] However, two or more alkenes can be derived from **6**, **8**, and **9**. The ratio of the alkene isomers from photolyses is compared with thermal reactions, which supports the α-cleavage/disproportionation hypothesis (Table 3).

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.

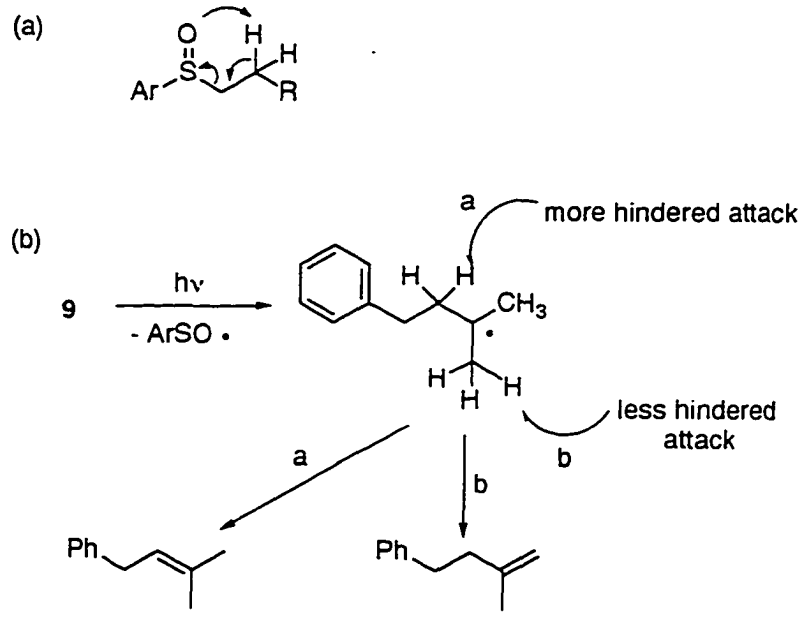


Figure 9. Mechanisms for (a) thermal and (b) photochemical formation of alkenes.

Table 3. Ratio of alkene products from degradation of **6**, **8**, and **9**.

Compound	Conditions	Product Ratio[a]
		$PhCH{=}CHMe$[b]$/PhCH_2CH{=}CH_2$
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.

When considering the thermolysis reactions, 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 non-conjugated 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 tri-substituted and disubstituted alkene, and the selectivity approaches one.

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 one. 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.

Intramolecular hydrogen abstraction

Compared to the hydrogen abstraction reactions of carbonyl compounds,[35] hydrogen abstraction by sulfoxides is not well established. It has been proposed, however, to account for the products of certain reactions.[11,42,43] 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 10). Such products, of course, are a matter of speculation before the experiment. The results of these photolyses, already presented in Table 1, do not include any of the speculative products in Figure 10.

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 4. All of the compounds from 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

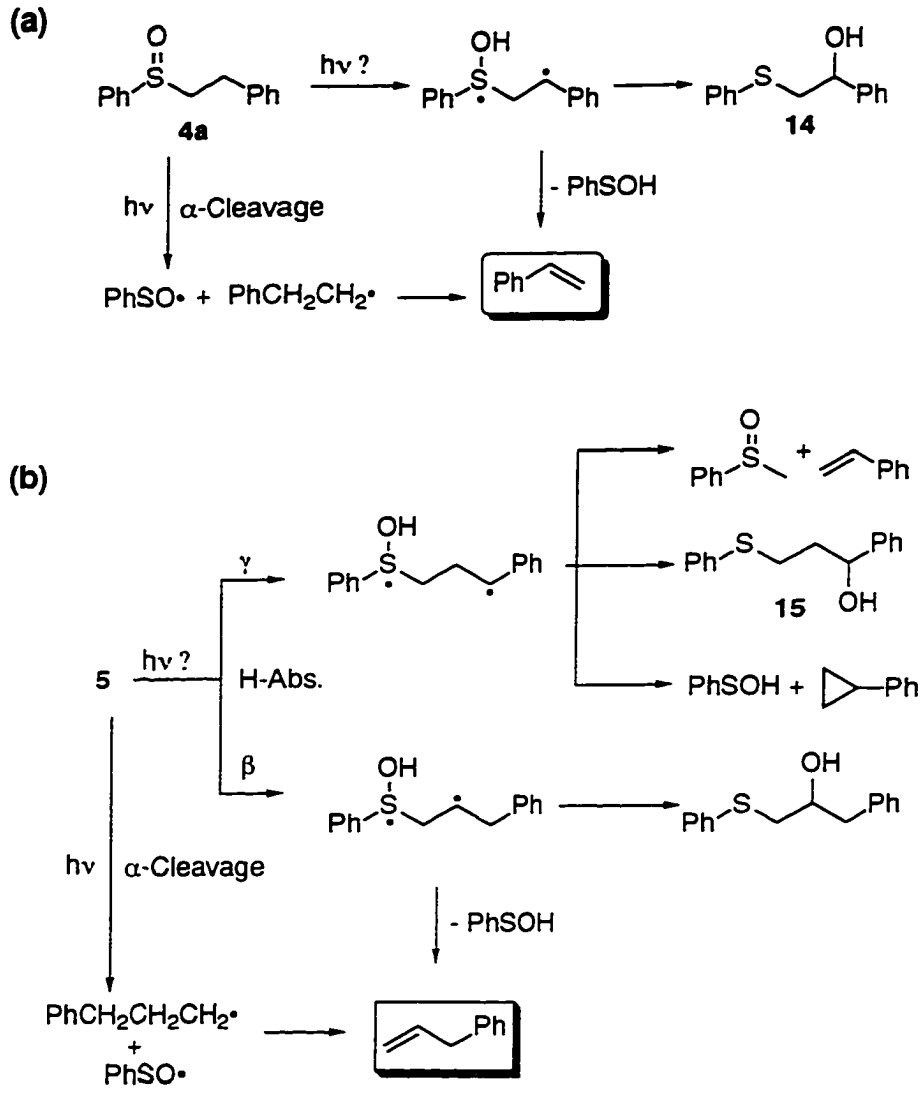


Figure 10. Postulated photochemistry of **4a** (a) and **5** (b) with hydrogen abstraction as a first step. Only the olefinic products in boxes are observed.

was possible (if unlikely, at such low conversions) that benzaldehyde might derive from secondary photolysis of **14** and the corresponding β-hydroxysulfides from **6** and **8**. Therefore **14** was synthesized and the independent photolysis 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.

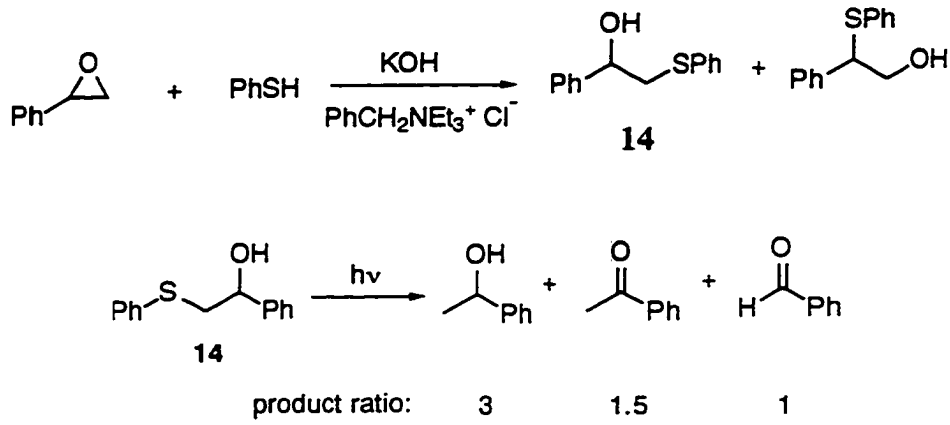


Figure 11. Synthesis and photolysis of **14**.

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 alcohols or phenones (*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 has a higher excitation coefficient at the irradiated wavelength (Figure 12). It is still

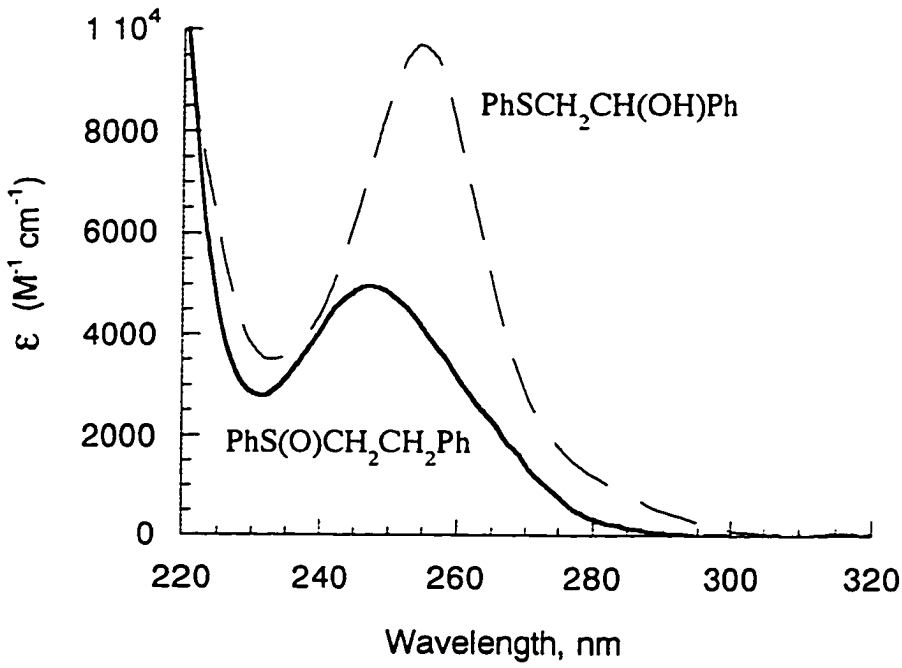


Figure 12. UV absorption spectra of **4** and **14** in acetonitrile.

unlikely 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 true, we might expect a significant difference in the quantum yields for the **3/4** and **8/9** pairs, because the benzylic hydrogens available for 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 the α-cleavage/disproportionation mechanism is much more likely.

Photolysis of *ortho*-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 re-ketonization process.[35] In many cases, this technique can be used to convert the CH_3 group to CD_3 nearly quantitatively. Analogous sulfoxides can be used to examine the intramolecular hydrogen abstraction reactions. Up to 12 hydrogen atoms might be exchanged in **13** and six in **12** (Figure 13). Sulfoxides **12** and **13** were photolyzed to 30–50% conversion in a mixture of 75% CH_3CN and 25% D_2O using a 300 nm Rayonet. The remaining starting material was examined by GC-MS. There was no evidence of deuterium

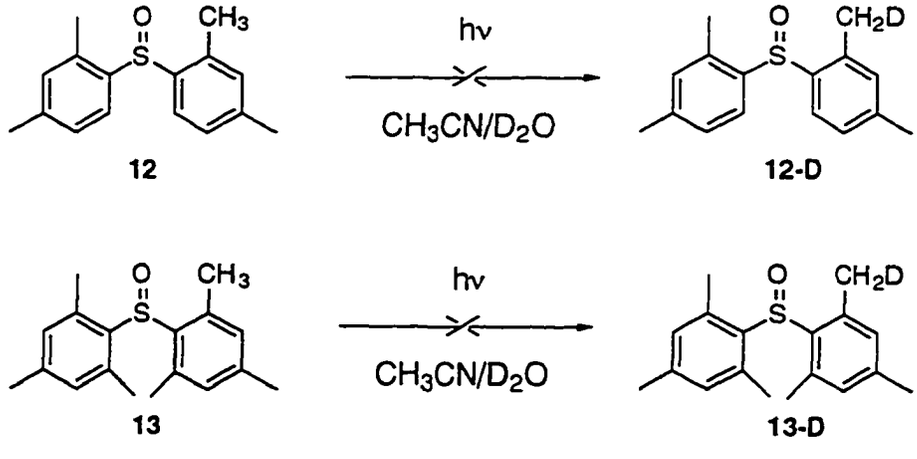


Figure 13. Photolysis of **12** and **13** in CH_3CN/D_2O mixture.

incorporation, and certainly not of multiple deuterium incorporation. Most of the photolysis products were from α-cleavage. Though negative evidence, such as reported here, does not rule out hydrogen abstraction as a primary process of sulfoxide excited states, it undoubtedly contributes to our skepticism.

From the present data we can only conclude that intramolecular hydrogen abstraction, if it really exists, is much less important comparing with C–S bond α-cleavage in the photolysis of aryl alkyl sulfoxides. Nor has it much effect on the racemization of these sulfoxides. This is very different from ketone photochemistry, where intramolecular γ-H abstraction plays a very important role. The possible reasons may include: (1) the electron density distribution difference between a C=O group and a S=O group; (2) a conformational difference which makes the S=O group less sterically favorable for hydrogen abstraction.

Thiosulfinate and thiosulfonate

Thiosulfinates **15** are the isolated form of corresponding sulfenic acids RSOH, as from the thermolysis of sulfoxides with β-hydrogen atoms.[38] They form by condensation with loss of H_2O. Thiosulfonates **16** and disulfides are further thermal decomposition products of arylthiosulfinates (Figure 14). On the other hand, thiosulfonates are formed by the combination of two sulfinyl radicals, which probably results from the rearrangement of *vic*-disulfoxide and/or *OS*-sulfenyl sulfinates (Figure 15).[44,45]

Thiosulfinate **15** is less stable than the corresponding thiosulfonate **16** both thermally and photochemically. In fact, phenyl benzenethiosulfonate $PhSO_2SPh$ is relatively quite stable. Its photolysis at 267 nm in acetonitrile has a quantum yield about 0.13 (phenyl benzyl sulfoxide has a quantum yield about 0.3 under the same conditions). Under oxygen saturation conditions, the photolysis quantum yield increased to about 0.2. The formation of the major products can be explained by Figure 16. Some of those reactions may also be thermally achievable. The thiyl and sulfonyl radical intermediates were observed from the e.s.r. spectroscopy study of some substituted arenethiosulfonates.[17,18]

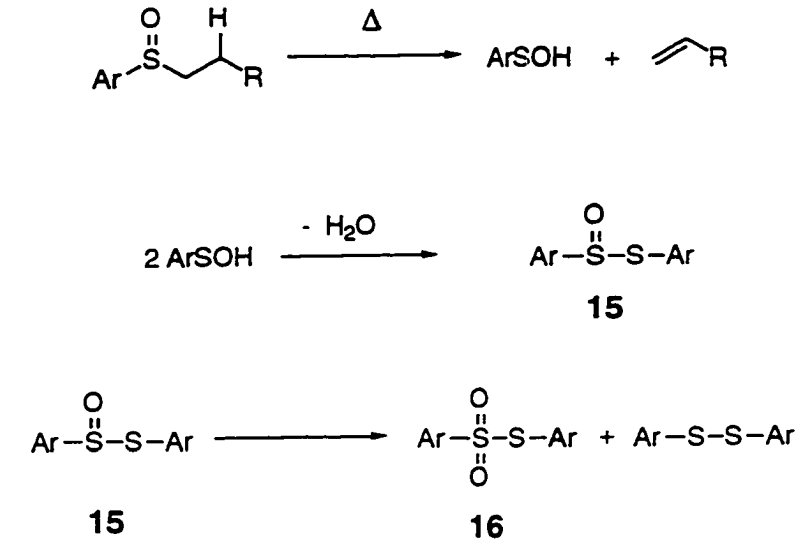


Figure 14. Formation and decomposition arylthiosulfinate **15**.

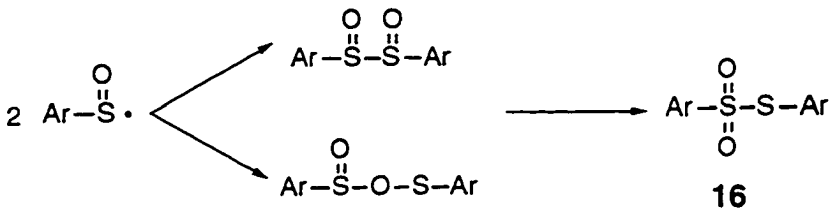


Figure 15. Arylthiosulfonate **16** formation from the combination of sulfinyl radicals.

The relatively high yield of thiosulfinate **15** in the photolysis of aryl *t*-alkyl sulfoxides suggests the existence of an arenesulfenic acid intermediate. It may come from either disproportionation between the aryl sulfinyl and alkyl radical pair or intramolecular β-hydrogen abstraction of the sulfoxide. If the former assumption is true, the hydrogen abstraction by the aryl sulfinyl radical from the alkyl radical must happen in the cage, otherwise thiosulfinate (from coupling of arylsulfinyl radicals) would be the major product. If this is the case, it will be difficult to tell the difference of the two assumptions because both have the same processes and gave the same products, the only difference is just the sequences (Figure 17). The olefin

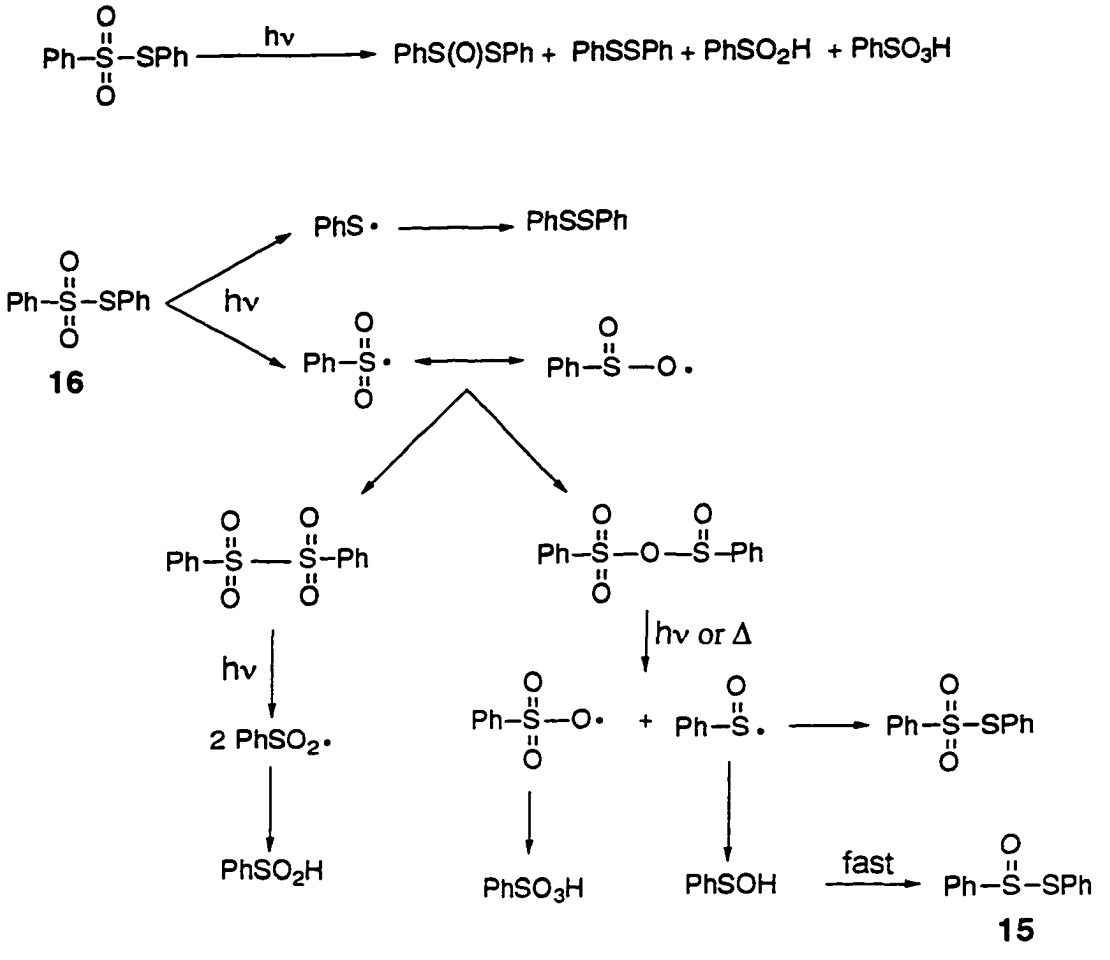


Figure 16. Products of arylthiosulfonate **16** photolysis.

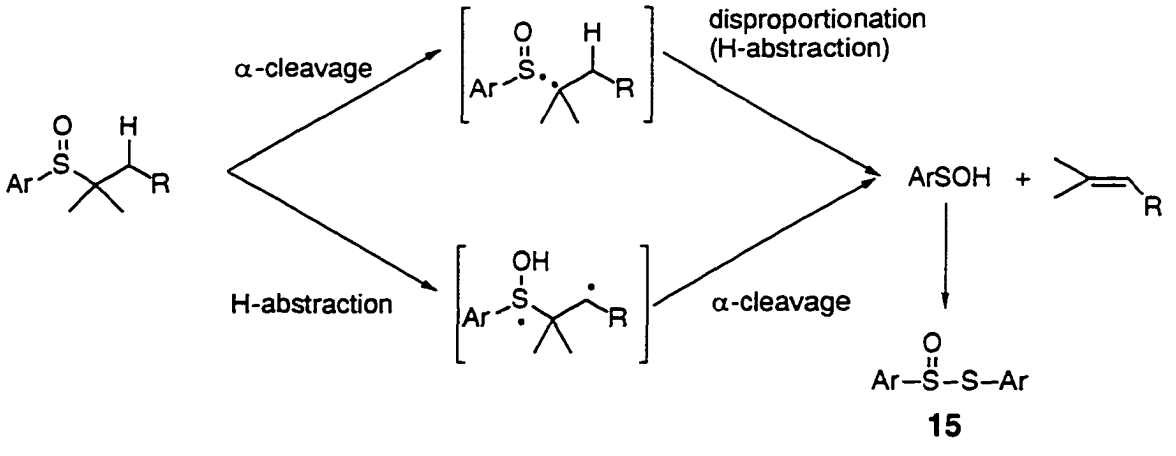


Figure 17. Proposed mechanisms of the formation of aryl thiosulfinate **15** and alkene.

regioselectivity analysis in section 6 supports the first (α-cleavage plus disproportionation) route. However, this does not allow us to rule out some possible contribution from the H-abstraction route.

Chiral sulfoxides and stereomutation

One of the most important features of sulfoxides is their chirality when the two substitutes are different groups. The racemization of sulfoxides under acidic[46] and thermolytic[47-49] conditions has been well studied. Based on activation parameters, it was assumed that thermochemical racemization for most diaryl, alkyl aryl and dialkyl sulfoxides took place by direct inversion of the stereocenter (pyramidal inversion) (Figure 18 (a)).[49] There are two exceptions: a sulfinyl-benzyl radical pair mechanism for aryl benzyl sulfoxides (Figure 18 (b))[48] and a concerted rearrangement for allylic sulfoxides (Figure 18 (c)).[47]

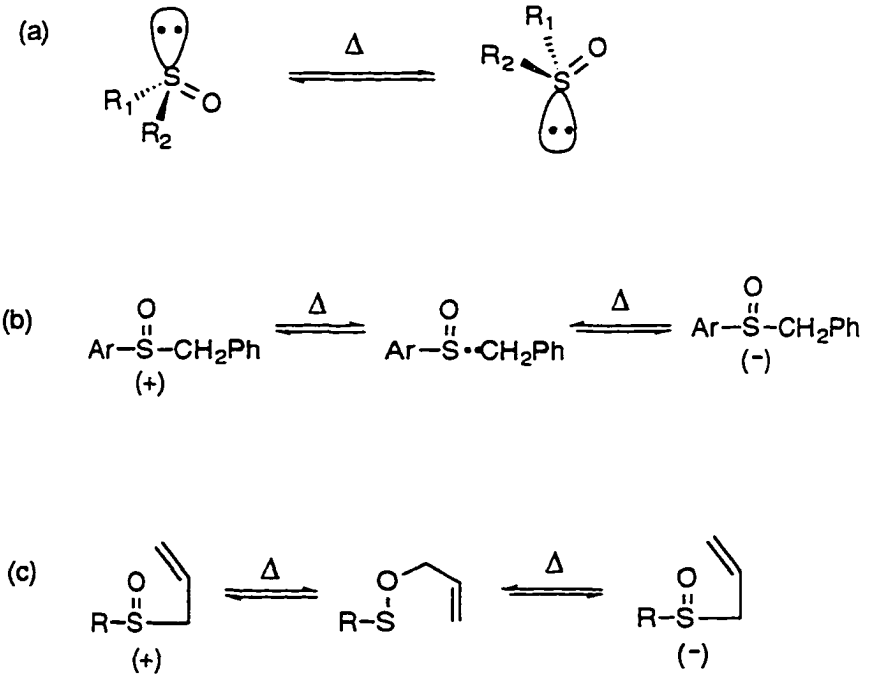


Figure 18. Thermal racemization mechanisms of various sulfoxides.

Photochemical (direct and sensitized) stereomutation of sulfoxides has been known for some time.[50-58] It has been suggested that the inversion of the sulfur center could take place directly or through homolytic α-cleavage and recombination. Certainly some stereomutation was by the cleavage/recombination mechanism, so the real questions are whether this mechanism is structure related and whether it can account for all of the racemization.

In our previous photolysis study of **1**, we proposed that homolytic α-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.)

Table 4. Quantum yields for loss of starting materials (in parentheses) and optical activity of chiral sulfoxides at 267 nm photolysis.

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

Photolysis of chiral sulfoxides in different solvents at 267 nm (concentration = 4–6 mM) shows that the primary alkyl aryl sulfoxides behave quite differently from **1**. Despite the very low values for Φ_{loss}, they have very high Φ_{rot} values. 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 also unlikely to be important due to 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 an 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 in methanol and ethylene glycol. These two solvents have very similar polarities (dielectric constants difference within about 15%, ε: CH_3OH 32.7, ethylene glycol 37.7), but the viscosity of the latter is more than 30 times higher. Although we favor an inversion mechanism for the stereomutation of **3** and **5**, a more detailed conclusion cannot be drawn at this time. Efforts continue in our laboratory to clarify this issue.

The racemization of **1** may occur by either a cleavage-recombination mechanism or by inversion. Two points 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-recombination is very rapid for this compound.

Flash photolysis study of sulfoxides

The work previously described in this chapter make a strong argument for the predominance of a-cleavage reactivity for these sulfoxide. However, direct evidence for the intermediacy of sulfinyl and alkyl radicals was lacking. Although alkyl radicals have been well characterized,[59] there is little information concerning the properties of sulfinyl radicals. The observation of arylsulfinyl radicals were claimed from some brief and qualitative EPR and CIDNP studies. A brief microsecond flash photolysis report on 4,4'-ditolyl and diphenyl sulfoxides showed a long-lived absorption assigned to the arylsulfinyl radical.[31]

In order to support our steady state α-cleavage mechanism, a series of sulfoxides were chosen for examination by ns-μs flash photolysis (Figure 12).[60]. A representative example, obtained from compound **1a** in cyclohexane is shown in Figure 13. This spectrum was obtained in the presence of oxygen, which removed the interference of carbon-centered radicals. The portion of the transient absorption spectrum with maxima at 300 and 450 nm is not affected significantly by change of the precursor sulfoxide, solvent, or the presence of

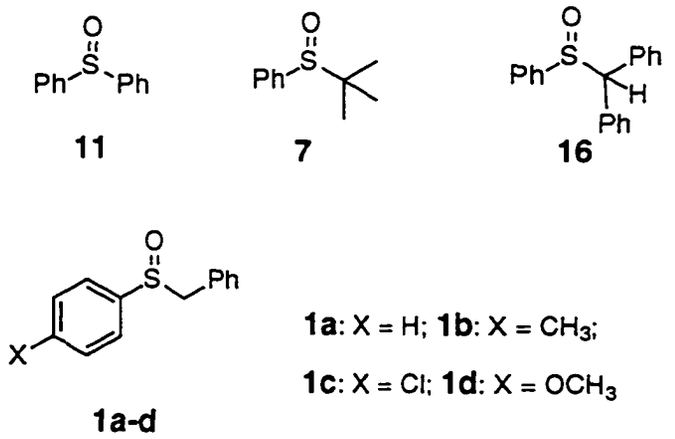


Figure 12. Sulfoxides for the flash photolysis study.

oxygen. The decay of the 300 nm transient was very well fit to second order kinetics and the initial intensity of the signal was proportional to the energy of the laser pulse. For all sulfoxide precursors in acetonitrile, the signal at λ_{max} = 300 nm decays with the same rate constant $2kr/\varepsilon = (5.6\pm0.3) \times 10^5$ cm s^{-1} and is assigned to the sulfinyl radical PhSO•.

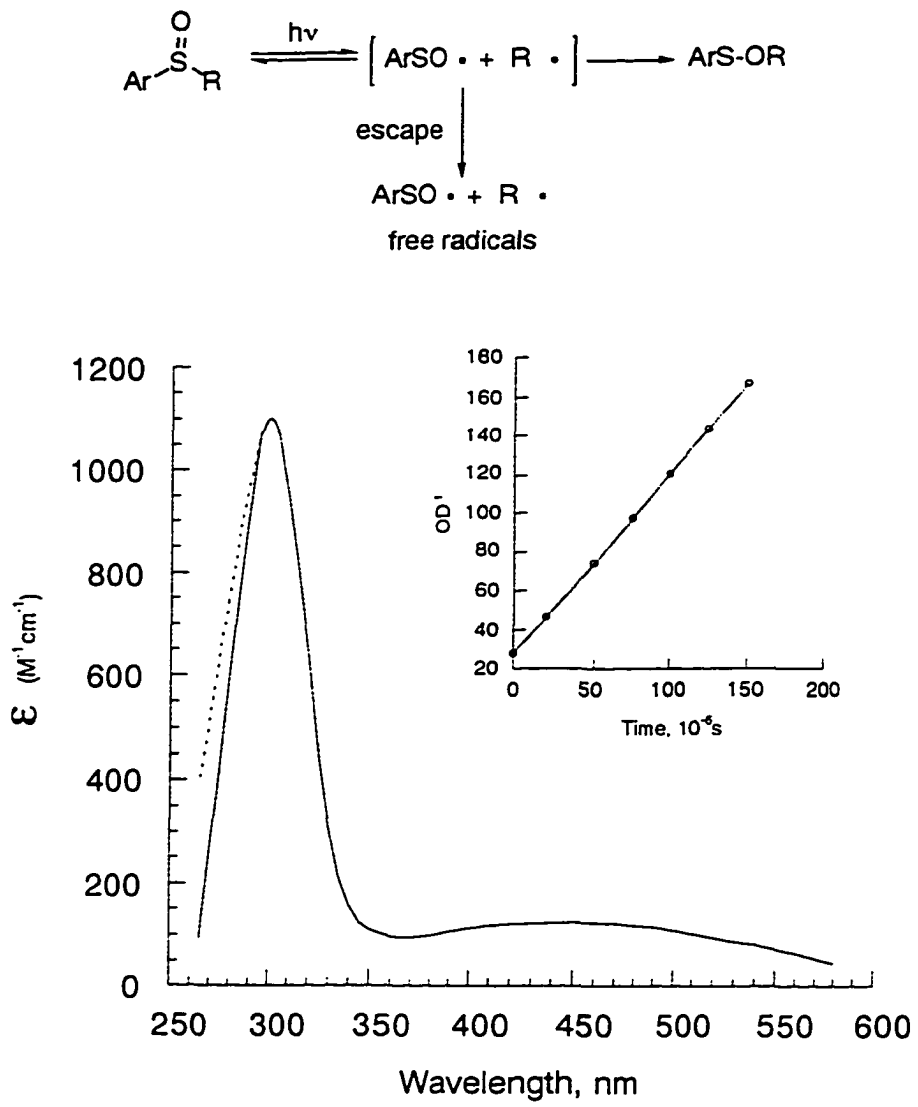


Figure 13. Absorption spectrum of PhSO• radical after excitation of **1a** (6.2×10^{-5} M) in air-saturated cyclohexane (solid line). Absorption spectrum of PhSO• corrected for ground state bleaching of sulfoxide (dashed line). Insert: Second-order plot of the decay kinetics at 300 nm in the same solution.

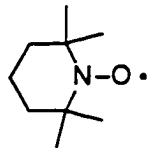
The quantum yield of PhSO• which escapes the solvent cage was measured in comparison with the triplet-triplet absorption of anthracene (Φ_T = 0.71 and $\varepsilon_{422.5}$ = 6.47 x 10^4 M^{-1} cm^{-1})[61,62] in degassed cyclohexane. The optical density at the excitation wavelength and the energy of the laser pulse (7 mJ) were equal for sulfoxide and anthracene solutions. Among the sulfoxides tested, the diphenylmethyl phenyl sulfoxide (**16**) shows the maximum quantum yield of free PhSO• (Table 5). The reasons may include both favorable cleavage and steric hindrance to recombination from the structural feature of **16**. This trend qualitatively coincided with the sulfoxide disappearance quantum yields in our steady state photolysis study.

Table 5. Quantum yields of phenylsulfinyl radical PhSO•

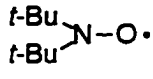
Sulfoxide	Solvent	$\Phi_{PhSO•}$
PhSOPh (**11**)	cyclohexane	0.06
PhSO(*t*-Bu) (**7**)	cyclohexane	0.12
$PhSOCH_2Ph$ (**1a**)	cyclohexane	0.11
$PhSOCHPh_2$ (**16**)	acetonitrile	0.18

Finally, as part of the confirmation of the transient assignment, the reaction of arylsulfinyl radicals with stable nitroxide radicals was studied. Both TEMPO and DTNB were used. Rate constants were found by a first order expression. The 300 nm transient reacts with these nitroxides with rate constants (k_{rxn}) of 9.4 x 10^8 $M^{-1}s^{-1}$ and 1.0 x 10^9 $M^{-1}s^{-1}$ respectively. Such high rate constants are very strong support for the radical nature

of the 300 nm transient. A series of aryl radicals has been prepared similarly and the results of this study are reported elsewhere.[59]



TEMPO



DTBN

$$k_{obs} = k_0 + k_{rxn}[NO\bullet]$$

Summary

In this paper, the studies of quantum yields and photochemical products have lead to a considerable increase in our understanding of the behavior of electronically excited sulfoxides. 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. 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.

The observation of the same transient from various sulfoxides and in a variety of solvents represents the most direct evidence for the intermediacy of a sulfinyl radical, which confirms the α-cleavage pathway for the photolysis of aryl alkyl sulfoxides.

According to classical photochemistry and photophysics, once the singlet state is formed,

it has four modes of deactivation: fluorescence, radiationless decay, intersystem crossing, and chemical reactions. A full understanding of the photochemistry depends on the precise knowledge of these fundamental processes. For instance, a long singlet lifetime may permit competition between photophysical processes and photochemical reactions. A knowledge of these respective rates will allow us to make predictions about the probability of photochemical reactions in a given compound.

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.

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); the 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 x 2.1mm) 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 Chemical Co.) was used as received. Diphenyl sulfoxide (**11a**, Aldrich Chemical Co.) was recrystallized from hexane before use. The preparations of the aryl benzyl sulfoxides **1**, dixylyl sulfoxide (**12**), and dimesityl sulfoxide (**13**) have been described.[9,23] Phenyl 2-phenylethyl sulfoxide (**4a**)[63] was prepared by hydrogen peroxide oxidation of the corresponding sulfide.[64] *t*-Butyl phenyl sulfoxide (**7**) was prepared in 65% yield from *t*-butyllithium and (*S*)-(–)-menthyl benzenesulfinate.[48,65] ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 9 H), 7.40–7.60 (m, 5 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. No attempt was made to assess optical purity.[66]

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.

Benzyl *p*-chlorophenyl sulfoxide (1c). This compound was prepared in analogy to phenyl benzyl sulfoxide by oxidation of the sulfide. ^{1}H NMR ($CDCl_3$) δ 4.10 (s, 2 H), 7.20–7.40 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 63.6, 125.9, 128.5, 128.6, 128.7, 129.2, 130.4, 137.4, 141.3.

The sulfide was prepared in near quantitative yield from the sodium arenethiolate (from arenethiol and sodium methoxide) and an equal amount of benzyl bromide in methanol. The crude product was purified by recrystallization from CH_2Cl_2-hexane mixture. ^{1}H NMR ($CDCl_3$) δ 3.98 (d, J = 12.6 Hz, 1 H), 4.10 (d, J = 12.6 Hz, 1 H), 6.97 (dd, J = 7.6, 1.6 Hz, 2 H), 7.24–7.42 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 39.4, 127.4, 128.7, 128.9, 129.1, 131.5, 132,5, 132.6, 134.8, 137.2.

Benzyl *p*-methoxyphenyl sulfoxide (1d). This compound was prepared in analogy to phenyl benzyl sulfoxide. ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3 H), 3.94 (d, J = 12.3 Hz, 1 H), 4.09 (d, J = 12.3 Hz, 1 H), 6.89–6.99 (m, 4 H), 7.20–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 55.6, 63.8, 114.4, 126.4, 128.2, 128.5, 129.4, 130.5, 133.7, 162.1.

The sulfide was synthesized the same as described above. ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3 H), 4.00 (s, 2 H), 6.80 (d, J = 8.7 Hz, 1 H), 7.20–7.30 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 41.3, 55.4, 114.5, 126.1, 127.1, 128.5, 129.0, 134.2, 138.2, 159.3.

***p*-Tolyl 2-phenylethyl sulfoxide (4b).** This compound was prepared in near quantitative yield by oxidation of the corresponding sulfide with excess H_2O_2 (30%) in ethanol. ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3 H), 2.85–3.15 (m, 4 H), 7.33 (d, J = 8.1 Hz, 2 H), 7.52 (d, J = 8.1 Hz, 2 H), 7.16–7.28 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 121.4, 28.2, 58.3, 124.0, 126.6, 128.5, 128.7, 129.9, 138.8, 140.4, 141.5.

The corresponding sulfide was prepared in 65% yield from *p*-thiocresol and 2-phenyl ethyl bromide in THF. ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3 H), 2.94 (t, J = 8.0 Hz, 2 H), 3.17 (t, J = 8.0 Hz, 2 H), 7.16 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2 H), 7.22–7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.0, 35.7, 35.8, 126.3, 128.4, 128.5, 129.7, 130.0, 132.5, 136.1, 140.3.

(*R*)-(+)-Phenyl 3-phenylpropyl sulfoxide (5). This compound was prepared in 40% yield from 3-phenylpropylmagnesium bromide and (*S*)-(−)-menthyl benzenesulfinate.[48,65] Repeated recrystallization from benzene-hexane gave a sample with constant melting point of 53.5–53.8 °C. A racemic sample has melting point of 44–45 °C. $[\alpha]^{20}_{405nm}$ = 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 2-phenylpropyl magnesium bromide and (*S*)-(−)-menthyl benzenesulfinate in anhydrous ether.[48,65] Separation of this colorless oil on silica led to variation of the ratio of diastereomers, but a single enantiomer could not be obtained, so the original mixture was used, bp 140 °C dec. 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[21]: 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.[20] 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 four hours, 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 = 1.5, 7.5 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**. ^1H 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. ^1H 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.

1-Phenyl-2-phenylthioethanol (14).[67] This compound was synthesized from the reaction of thiophenol and styrene oxide in the presence of a phase transfer catalyst. To the mixed solvent of 15 ml of water and 20 ml of benzene, 1.2 g (10 mmol) of styrene oxide, 1.3 g (12 mmol) of thiophenol, 0.8 g (14 mmol) of KOH and 0.1 g of triethylbenzylammonium chloride were added. Under an argon atmosphere, the mixture was stirred vigorously at room temperature for 48 hours. The mixture was extracted with ether, and the organic layer was washed with 10% NaOH and brine. **14** (R_f = 0.52) was separated from another major product 2-phenyl-2-phenylthioethanol (R_f = 0.4) by silica column chromatograph. Compound **14**, ^1H NMR ($CDCl_3$) δ 2.90 (d, J = 3.0 Hz, 1 H), 3.10 (dd, J = 13.5, 10.5 Hz, 1 H), 3.33 (dd, J = 13.5, 3.0 Hz, 1 H), 4.73 (m, 1 H), 7.20–7.45 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 44.0, 71.6, 125.8, 126.8, 128.0, 129.1, 130.2, 134.9, 142.1. IR (KBr) 3409 (broad), 3058, 2918, 1581, 1479, 1437, 1024, 737, 698 cm^{-1}. 2-Phenyl-2-(phenylthio)ethanol: ^1H NMR ($CDCl_3$) δ 2.07 (s, broad, 1 H), 3.90 (m, 2 H), 4,30 (t, J = 6.8 Hz, 1 H), 7.21–7.35 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 55.9, 65.1, 127.5, 127.8, 128.0, 128.7, 128.9, 132.5, 133.7, 138.9.

1-Phenyl-3-phenylthio-1-propanol (15).[68] This compound was prepared by literature method.[69] 2.5 g (20 mmol) of $PhSCH_3$ was dissolved in 30 ml of anhydrous THF.

9 ml (50 mmol) of HMPA was added. After this solution was cooled to – 60 °C, *n*-BuLi (24 mmol) solution (Aldrich Chemical Co.) was added dropwise. The reaction was kept stirring at this temperature for about 4 hours. Then 2.4 g (20 mmol) of styrene oxide was added. The reaction was warmed up to room temperature, and the reaction continued for about 40 hours. The reaction was then quenched with 10 ml of water and extracted with 30 ml of ether three times. The organic layer was collected and washed with brine three times and the product was purified by silica chromatograph to afford a cream white solid in 75% yield (R_f = 0.4, ethyl acetate/hexane = 20/80). ^{1}H NMR ($CDCl_3$) δ 1.93–2.17 (m, 3 H), 3.01 (t, J = 7.2 Hz, 2 H), 4.87 (dd, J = 8.1, 5.1 Hz, 1 H), 7.14–7.37 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 29.9, 38.1, 73.0, 125.8, 125.9, 127.7, 128.5, 128.9, 129.2, 136.1, 143,9.

Phenyl diphenylmethyl sulfoxide (16). The sulfoxide was prepared in 60% isolated yield by oxidation of the sulfide with the urea-hydrogen peroxide complex.[21] The crude product was purified by recrystallization from CH_2Cl_2-hexane mixture. ^{1}H NMR ($CDCl_3$) δ 4.80 (s, 1 H), 7.23–7.39 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 77.8, 125.0, 128.2, 128.6, 128.8, 129.3, 129.7, 131.1, 134.1, 135.5, 142.9.

The sulfide was prepared by modification of the method of Finzi and Bellavita.[70] Benzhydrol (11g, 59 mmol) was dissolved in 75 ml of acetic acid and 25 ml of sulfuric acid at room temperature. To this mixture thiophenol (59 mmol) was added in a dropwise fashion. After 2 hours of stirring, the mixture was filtered and the precipitate was washed with water, then dried under vacuum. The sulfide was obtained in near quantitative yield and was used without further purification. ^{1}H NMR ($CDCl_3$) δ 5.53 (s, 1 H), 7.40 (d, J = 7.2 Hz, 4 H), 7.12–7.30 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 57.3, 126.5, 127.2, 128.4, 128.5, 128.7, 130.4, 136.1, 141.0.

Sulfenic esters. Appropriate sulfenic esters were prepared by reaction of alcohols with benzenesulfenyl chloride or *p*-toluenesulfenyl chloride in the presence of triethylamine.[48] 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 their 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.[71,72] Phenyl benzenethiosulfinate and *p*-tolyl *p*-toluenethiosulfinate were also prepared by a literature method.[73] 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.[74] The pure compounds were obtained by silica column chromatograph of the disulfide mixtures. 2-Methyl-4-phenyl-2-butene was obtained from thermolysis of **9**. ^1H 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, 1.5 Hz, 1 H), 7.15–7.32 (m, 5 H).

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

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. All solution photolyses were carried out with magnetic stirring and after argon flushing to remove oxygen. Unless otherwise noted, starting concentrations of 3–6 mM were used.

Solid photolysis experiments were carried out by dissolving about 10 mg of sample in methylene chloride. This solution was used to coat the inside wall of a quartz tube with the solid material then blanketed with argon under a septum. This tube was photolyzed inside the modified RMR-500 "mini-Rayonet" from Southern New England Ultraviolet with a cooling fan which keeps the sample at ambient temperature. The 254 nm mercury lamps were used. The solid was then dissolved in acetonitrile and analyzed by HPLC.

Laser flash photolysis. All experiments were carried out using a Macintosh controlled nanosecond transient absorption spectrometer with Labview 2 software. The samples were irradiated with the 4th harmonic of a Nd:YAG laser (266 nm, 5 ns, 2–25 mJ/pulse, 3 mm beam radius). The spectroscopic detection system includes a pulsed 75 W xenon lamp ($\tau \sim 1$ ms), an ISA H10 monochromator, an 1P-28 photomultiplier, and a Textronix TDS-250 200 MHz transient digitizer. The optical density of solutions in the 1 x 1 x 5 cm quartz cell is ~ 0.3 at 266 nm. The accuracy of quantum yields, excitation coefficient, and rate constants is estimated to be ±20%.

Quantum yields. Quantum yields were determined using the PTI lamp. The actinometer was azoxybenzene.[75] Quantification was done with HPLC. *p*-Xylene or 1-phenylundecane were used as internal standards. Sample and actinometer cells were sequentially irradiated and the latter was 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 an 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 Chemical Co., 99%) as internal

standard 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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(1) Some of the results in this chapter were published in *J. Org. Chem.* **1997**, *62* 857-864, and are reproduced with permission from the American Chemical Society.
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CHAPTER V

THERMOLYSIS OF ARYL ALKYL SULFOXIDES: KINETICS AND REGIOSELECTIVITY

A paper prepared for the *Journal of Organic Chemistry*

Yushen Guo and William S. Jenks

Abstract: The thermolyses of aryl alkyl sulfoxides under different conditions are described. All reactions in both gas phase and solutions display first-order kinetics. The regioselectivity of alkene products from both thermal and photo processes are compared. The production of alkane as minor product and different kinetic profiles at higher temperatures support the possible existence of a homolytic α-cleavage mechanism at high temperature thermolysis, along with a classical concerted cyclic elimination mechanism. Pulsed stirred-flow thermolysis and direct GC injector *in situ* pyrolysis methods have been used to study the thermal elimination regioselectivity and activation parameters of these sulfoxides at high temperature.

Introduction

Thermal or base-catalyzed elimination reactions have been widely used in the synthesis of alkenes. Different precursors have been used, such as esters, xanthates, quaternary ammonium hydroxides, amine oxides, and sulfonium compounds.[1-5] Sulfoxides and sulfones can be converted to olefins by thermolysis or base-catalyzed β-elimination.[6] Recently, the thermolysis of neat methyl alkyl sulfoxides has been used in the synthesis of 1,1-difluoroolefins which are used as intermediates to other biologically active molecules, such as enzyme inhibitors.[7] Microwave irradiation has also been used to enhance the β-elimination of sulfoxides with other functional groups.[8]

The thermochemistry and kinetic study of sulfoxides have further significance. It has been found that the thermal properties of sulfoxides are related to their peroxide-decomposing ability and their efficiency as thermal antioxidants.[9] These are the materials that promote the decomposition of organic hydroperoxides to form stable products, which frequently function as preventive antioxidants in polymers.[9] It has been proposed that the thermolysis mechanism determines if a specific sulfoxide could be used as antioxidant or peroxide decomposer. Instability of the sulfoxides appears to be an important requirement for their activity as oxidation inhibitors. Further understanding of the mechanism by which sulfoxides function as stabilizers against thermal auto-oxidation clearly requires additional information about the decomposition of sulfoxides and the analyses of products. Also, this study is important as part of a general investigation which may be applied to the design of new desulfurization processes of organosulfur compounds present in the crude oil and coal.[10]

Generally, there are three kinds of reactions related to the thermolysis of sulfoxides: homolytic α-cleavage, concerted elimination, and racemization.[11-14] The pathway and products depend on the structure of the sulfoxides and the thermolysis temperature. In addition to stereomutation, sulfoxides without β-hydrogen have been shown to go through a homolytic S-C bond cleavage with the possible formation of a sulfenic ester intermediate which cannot survive the thermolysis conditions and gives further decomposition products.[13,15] Research has been done on the high temperature pyrolysis of dimethyl sulfoxide in the gas phase,[16,17] and a homolytic α-cleavage free radical mechanism was proposed (ΔH°_{298} = 54 kcal/mol).

The sulfoxides with β-hydrogens predominantly undergo a *syn*-β-elimination to form alkenes and sulfenic acids (usually isolated as thiosulfinates). At high temperature, a radical process has also been proposed to account for olefin formation in some cases. In a study of the thermolysis of *trans*-2-butene episulfoxide, Baldwin and coworkers[18] found a lower activation energy *cis*-elimination path at 35 °C, where over the temperature range 200–340

°C, the intermediate in the high activation energy path leading to the 2-butenes and SO is a biradical species with limited internal rotation (Figure 1).

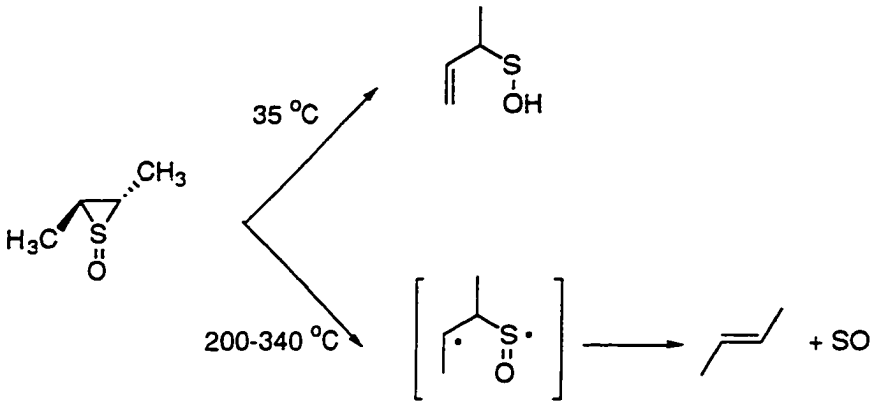


Figure 1. Thermolysis of *trans*-2-butene episulfoxide.

Kingsbury and Cram studied the thermolysis of diastereomeric 1,2-diphenyl-1-propyl phenyl sulfoxides at 80 °C and 120 °C.[19] At low temperature their results were consistent with the five-centered cyclic transition state mechanism. At higher temperature, however, a radical pair was formed which disproportionated by hydrogen atom transfer to yield predominantly the more thermodynamically stable alkene product (Figure 2).

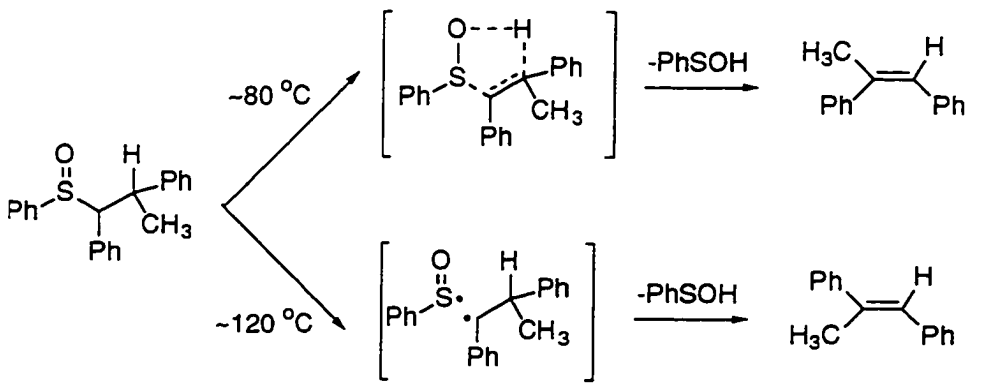
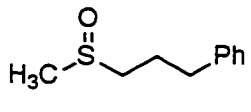


Figure 2. Thermolysis of 1,2-diphenyl-1-propyl phenyl sulfoxide.

Generally speaking, there is still very limited evidence for the radical mechanism. It has been claimed to not exist even in favorable sulfoxide cases.[20] We have studied the thermolysis of several sulfoxides with different structures. In each case, only one side of the sulfoxide has β-hydrogen atoms and also a phenyl group is attached for easy detection. The thermolysis of sulfoxides **1–3** was studied to examine the effect of methyl, vinyl and phenyl groups on the elimination kinetics to compare the transition state of the elimination reactions. Sulfoxides **4–6** were chosen as part of our comparative research on the photochemistry and thermochemistry of alkyl aryl sulfoxides,[21] especially the regioselectivity difference between the two processes. We studied their thermolysis in both solution and gas phase, which all show good first order kinetics. The product ratios and regioselectivity of the alkene isomers from these conditions are also compared, along with those obtained in the neat state thermolysis and photolysis.



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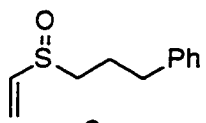

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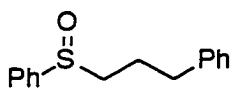

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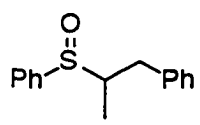

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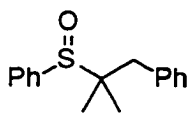

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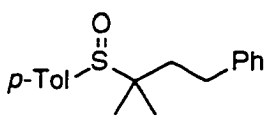


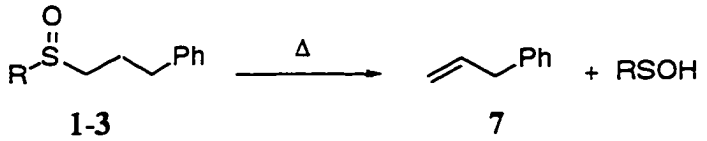
6

Results and Discussion

Thermolysis products

Thermolyses of sulfoxides **1–3** (Figure 3) gave a common olefin **7** in addition to corresponding sulfenic acids, which are all thermally unstable and eventually form other decomposition products. In a study of the thermolysis of sulfoxides **4–6** (Figure 4), the

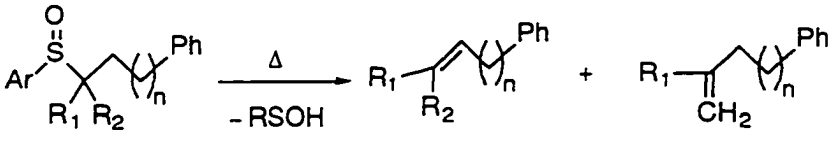
corresponding alkene isomer mixtures were the major products, besides the corresponding thiosulfinates (from sulfenic acid). The thiosulfinate was usually detected as a mixture of disulfide and thiosulfonate after prolonged heating.[22] Though the reaction products were not actually isolated, the products were identified by comparing their HPLC and/or GC trace with those of authentic samples. Data for compounds **4-6** are shown in Tables 1-3.



1-3 **7**

R=CH_3, CH_2=CH, Ph

Figure 3. Thermolysis and products of sulfoxide **1-3**.



4-6 **8a-8c** **9a-9c**

a. R_1=Me, R_2=H, n=0

b. R_1=Me, R_2=Me, n=0

c. R_1=Me, R_2=Me, n=1

Figure 4. Thermolysis and products of sulfoxide **4-6**.

Regioselectivity of alkenes

In most practical sulfoxide thermolyses, only one alkene is produced, which is desired from the synthetic aspect. However, when there are at least two different accessible β-hydrogen atoms, thermolysis elimination can give olefin isomer mixtures. Optically pure sulfoxides have been used to control the regioselectivity in steroidal sulfoxide eliminations.[23]

Chiral olefin compounds were also synthesized by the thermolysis of optically pure sulfoxides.[24] It should be noticed that at a higher temperature the stereospecificity could be lost with increased portion of radical mechanism.[19]

The regioselectivity of the olefin products from the thermolyses of **4** - **6** under different conditions were studied. They are compared with related photochemical processes. All photolysis experiments in solution used 267 nm irradiation of a 150 W Xe lamp filtered through a monochrometer setup. The ratios of alkene products were measured by HPLC. except in the direct "GC injector" experiments. The ratio of alkene products are given in Tables 1–3 with statistically adjusted selectivity in parentheses.

Table 1. Olefinic product ratios[a] from degradation of **4**.

Condition	$PhCH{=}CHCH_3$ (**8a**)[b]/$PhCH_2CH{=}CH_2$ (**9a**)
Δ, Methylcyclohexane, 81 °C	13.2 (19.8)
Δ, *t*-BuOH, 80 °C	12.7 (19.1)
Δ, Neat, 150 °C	12.3 (18.5)
Δ, GC injector, 220–300 °C	3.7–2.8 (5.6–4.2)
hv, Methylcyclohexane	1.43 (2.1)
hv, *t*-BuOH	0.72 (1.1)
hv, Acetone	0.60 (0.90)

(a) Statistically adjusted selectivity given in parentheses. (b) sum of E and Z isomers.

Table 2. The ratio[a] of olefinic products from degradation of **5**.

Condition	$PhCH{=}CMe_2$ (**8b**)/$PhCH_2CMe{=}CH_2$ (**9b**)
Δ, Methylcyclohexane, 90 °C	0.91 (2.7)
Δ, GC injector, 220–300 °C	0.89–0.87 (2.7–2.6)
Δ, *t*-BuOH, 80 °C	0.63 (1.9)
Δ, *t*-BuOH or CH_3CN for 70 days[b]	0.57 (1.7)
Δ, Neat, 90 °C	0.43 (1.3)
hv, *t*-BuOH	0.18 (0.54)
hv, CH_3CN	0.16 (0.48)
hv, Neat (254 nm Rayonet)	0.10 (0.30)

(a) Statistically adjusted selectivity given in parentheses. (b) room temperature.

There are several points which can be drawn from Tables 1–3. First, the regioselectivity for sulfoxide **4** is quite different from **5** and **6**. Sulfoxide **4** is a nearly 1:1 mixture of two diastereomers which was prepared from the reaction of 2-phenylpropylmagnesium bromide and (*S*)-(–)menthyl benzenesulfinate.[21] Thermolysis of **4** should give a **8a/9a** ratio approximately 2/1 statistically, while thermolysis of **5** would give a ratio of 2/3 (**8b/9b**) (Figure 5).

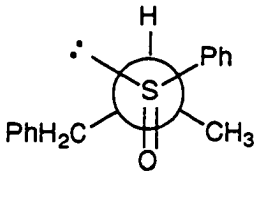
Sulfoxide **4** has two benzyl β-hydrogen atoms. This could lower the *cis*-elimination transition state. The conjugated olefin **8a** has an extra advantage over the terminal olefin **9a**.

One less α-methyl group in **4** compared to **5** might enhance β-hydrogen abstraction because of the decreased steric barrier for the transition from the staggered conformation to the eclipsed conformation in order to achieve the necessary distance between the O atom and the H atom (Figure 5).

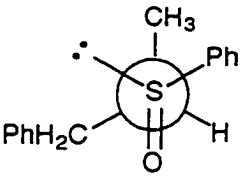
Table 3. The ratio[a] of olefinic products from degradation of **6**.

Condition	$PhCH_2CH{=}CMe_2$ (**8c**)/$Ph(CH_2)_2CMe{=}CH_2$ (**9c**)
Δ, GC injector, 220–320 °C	0.43–0.44 (1.28–1.31)
Δ, Methylcyclohexane, 81 °C	0.43 (1.28)
Δ, *t*-BuOH, 80 °C	0.39 (1.17)
hν, Methylcyclohexane	0.28 (0.84)
hν, Hexane (254 nm Rayonet)	0.22 (0.66)
hν, *t*-Butanol	0.13 (0.39)

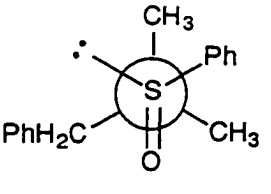
(a) Statistically adjusted selectivity given in parentheses.



4 (R, S)



4 (R, R)

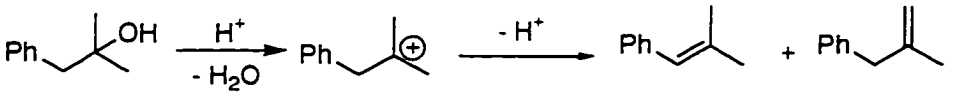


5

Figure 5. Conformation analysis of **4** and **5**.

A second observation is that both thermolysis and photolysis in the neat state gave relatively more terminal olefins. In the photolysis case, this could be because the steric effect is more important as the molecular mobility decreased. As in the thermolysis condition, the reason may also be the reversibility of elimination reaction – olefin **8** is more active in back reaction than **9**. Another observation is that protonic solvent gave more terminal olefins. This can be explained by the hydrogen bond to the oxygen of sulfoxides, which causes more steric hindrance and results in a higher yield of terminal alkene.

It is interesting to compare the alkene regioselectivities among the photochemical radical process, the concerted thermolysis, and other reactive intermediates. The acid catalyzed dehydration of 1,1-dimethyl-2-phenyl-ethanol (**10**) at ~ 180 °C was studied. This reaction goes through an E1 carbocation mechanism (Figure 6). The regioselectivity is between that observed from thermal and photochemical elimination of the sulfoxides (Table 2).



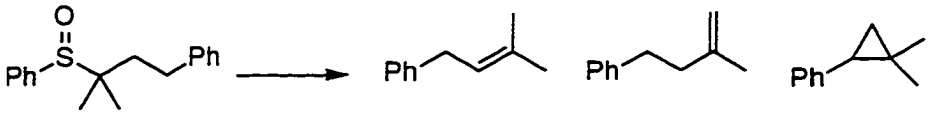
10 **8b** **9b**

8b/9b
0.25 (0.75)

Figure 6. Alkene isomer ratio from acid-catalyzed ($KHSO_4$) dehydration of neat tertiary alcohol. Statistically adjusted selectivity given in parentheses.

Sulfoxide **6** is a more proper example for comparison of the regioselectivity between a primary carbon center and a secondary carbon center. After the statistical adjustment, the regioselectivity of the thermal reaction is near unity, with a slight preference for the more thermodynamic stable alkene **8c**. Also the steric effect of the benzene ring in **6** is less important as it moves remote comparing to the benzene ring in **5**.

Interestingly, Babin and coworkers reported the production of olefins from a similar sulfoxide by base-elimination (Figure 7).[25] They also detected a minor cyclopropane-containing compound **12** under some basic conditions, which is not detected under either the thermal or photochemical conditions by us. An E_2 mechanism was proposed for the based-catalyzed sulfoxide elimination reactions.[26] The regioselectivity of the alkene products is more similar to the thermal process than the photochemical process (Table 3).



	11	**8c**	**9c**	**12**	**8c/9c**
$NaNH_2/NH_3(l)$		27	73	0	0.37 (1.11)
n-BuLi, TMEDA, hexane		26	67	7	0.39 (1.17)

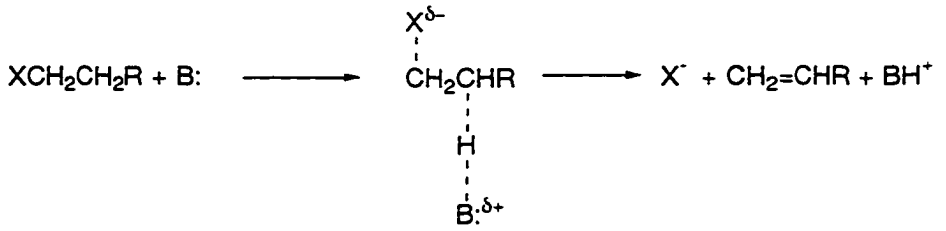
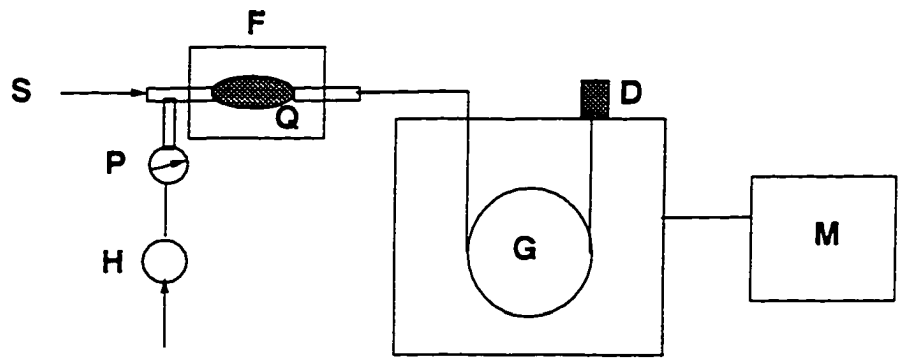


Figure 7. Elimination reaction of sulfoxide under basic conditions, which gave a regioselectivity between thermal and photochemical reactions, but closer to the thermal reaction. The statistically adjusted selectivity is given in parentheses.

Comparative kinetic study of sulfoxides 1-3

Gas phase thermolysis kinetics studies have been used in the study of DMSO[16] and some small cyclic sulfoxides.[27] Because of the relatively low stability of many sulfoxides with β- hydrogens and their low volatility, most other studies were done in solution. We have attempted to study the gas phase kinetics of sulfoxides **1–3** in order to provide data

which may be compared to quantum chemical calculations to examine the effects of substituents. The stirred-flow technique has been widely used in the kinetic study of various gas phase reactions.[28] It has some limitations, such as the need for more reactant to maintain constant flow concentration, and being more suitable for reactions at low conversion. The pulsed stirred-flow reactor was introduced latter where only a small amount of sample is needed.[29] We carried out the gas phase kinetic studies of some of the sulfoxides using a simplified pulsed stirred-flowed system (Figure 8).



S, Sample injector

Q, Quartz reactor

P, Pressure gauge

G, GC

H, He flow controller

D, FID detector

F, Furnance with temperature controller

M, Micro computer

Figure 8. Block diagram of pulsed stirred-flow thermolysis system.

The initial investigation showed that it is very critical to control the temperatures in this system. First is the furnace (**F**) temperature (also related to the thermolysis temperature in **Q**). We found there is a limited temperature range that can be used for these reactions (about 220–290 °C for **1** and **2**). Below this temperature sample cannot get out of the furnace completely. Above this temperature, almost no reactant left due to extensive decomposition.

The second temperature is the line between furnace and the GC column (**Q** to **G**). It was found that all the reactant and product can pass through the line without chemical change around 130 °C. The third temperature is the GC temperature. We use a gradient program (60 –180 °C) to keep the on column decomposition to a minimum. The adjustment of these three temperatures depends on the stability (or structure) of the sulfoxide under study. The more unstable the sulfoxide, the more difficult it is to find a suitable temperature combination. In fact, we failed to find suitable conditions for the more reactive phenyl 3-phenylpropyl sulfoxide (**3**); so it was studied in solution to compare with the other two sulfoxides. The logarithmic forms of Arrhenius equation and transition state theory (TST) equation are plotted (Figure 7). The reaction activation parameters are shown in Table 4.

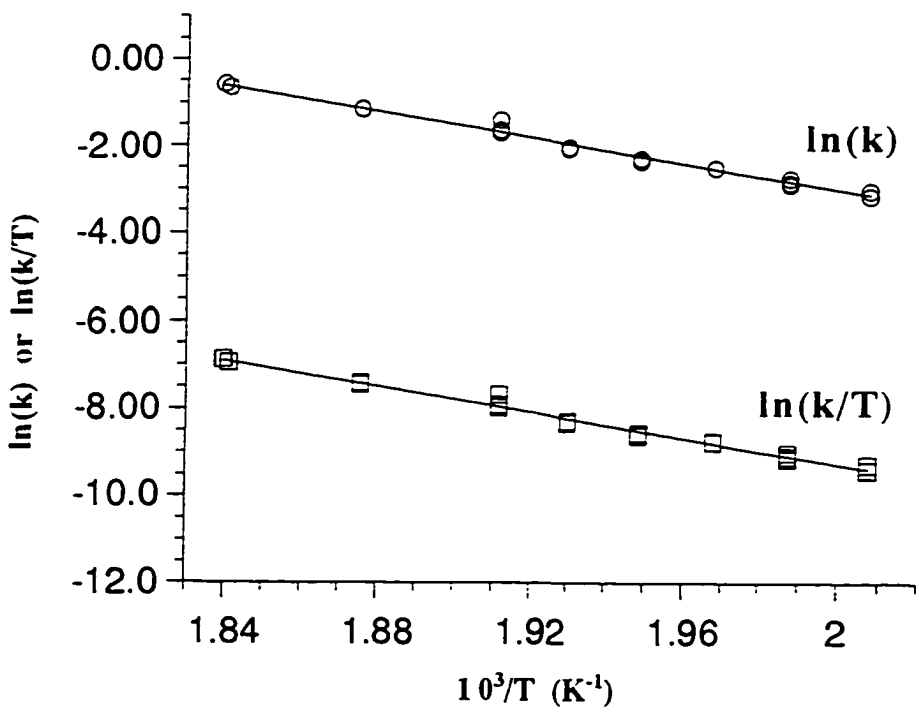


Figure 7. Plots of ln(k) and ln(k/T) for the stirred-flow thermolysis of **2** against temperature (225–270 °C). The error bars (≤ ± 0.1) are smaller than the size of the data markers.

Table 4. The kinetic data for the pulsed stirred-flow thermolysis of **1** and **2**.

Sulfoxide	**1**	**2**
Temperature (°C)	240–300	225–270
log(A)	12.5 ± 0.3	12.1 ± 0.3
Ea (kcal/mol)	34.0 ± 0.9	30.8 ± 0.8
$\Delta H^{\ddagger}$ (kcal/mol)	32.9 ± 0.9	29.8 ± 0.8
$\Delta S^{\ddagger}$ (cal/mol K)	− 4.5 ± 0.8	− 6.5 ± 0.8

Table 5. The kinetic data for the thermolysis of **1**, **2**, and **3** in decahydronaphthalene.

Sulfoxide	**1**	**2**	**3**
Temperature (°C)	150–165	140–160	135–160
log(A)	10.4 ± 0.7	12.5 ± 0.3	8.6 ± 0.8
Ea (kcal/mol)	29.0 ± 0.6	31.5 ± 0.6	23.7 ± 1.6
$\Delta H^{\ddagger}$ (kcal/mol)	28.2 ± 0.6	30.7 ± 0.6	22.8 ± 1.6
$\Delta S^{\ddagger}$ (cal/mol K)	− 13.8 ± 1.6	− 2.0 ± 1.5	− 21.9 ± 3.8

The thermolysis of sulfoxides **1-3** in decahydronaphthalene solution was also studied in order to compare their reactivities. The temperature ranges used are mostly determined by the reaction rate and the time scale for each HPLC run. The kinetic data are listed in Table 5. The negative entropies support the dominant concerted mechanism. Generally the data support the reactivity order of sulfoxide substituents: phenyl > vinyl > methyl. One needs to keep in mind the effect of reverse reactions between sulfenic acids and alkenes on the kinetic measurement, which is more likely important in solution thermal elimination reaction than in gas phase.

There are very little kinetic data in the literature about these three sulfoxides for us to compare the reliability of our results. The thermolysis activation energy of **1** was reported[30] to be about 32 ± 3 kcal/mol at about 145 °C in diglyme, which seems to fit well with our result.

Thermolysis kinetics in solution

As was mentioned before, sulfoxides **4–6** are too thermally unstable to be studied by the pulsed stirred-flow technique. Their thermolysis kinetics were studied in solution. The rates of decomposition were determined by following the concentration of sulfoxides and alkenes by HPLC. First-order kinetics were observed in the thermolysis of all three sulfoxides in both alcohol and alkane solvents. Figure 8 is a typical example of reaction profile. The rates in alcohol solvents were always slower than those in alkane solvents at the same temperature. This has been observed by other researchers and was rationalized by the steric effect caused by hydrogen bonds.[19]

Figure 9 clearly suggests the kinetics of possible mixed mechanisms for compound **4**. Higher temperature gave a larger $\Delta H^{\ddagger}$ and a larger $\Delta S^{\ddagger}$, which implied a mechanistic change to a less concerted process – evidence for a possible radical pair mechanism at higher temperature (Figure 10).

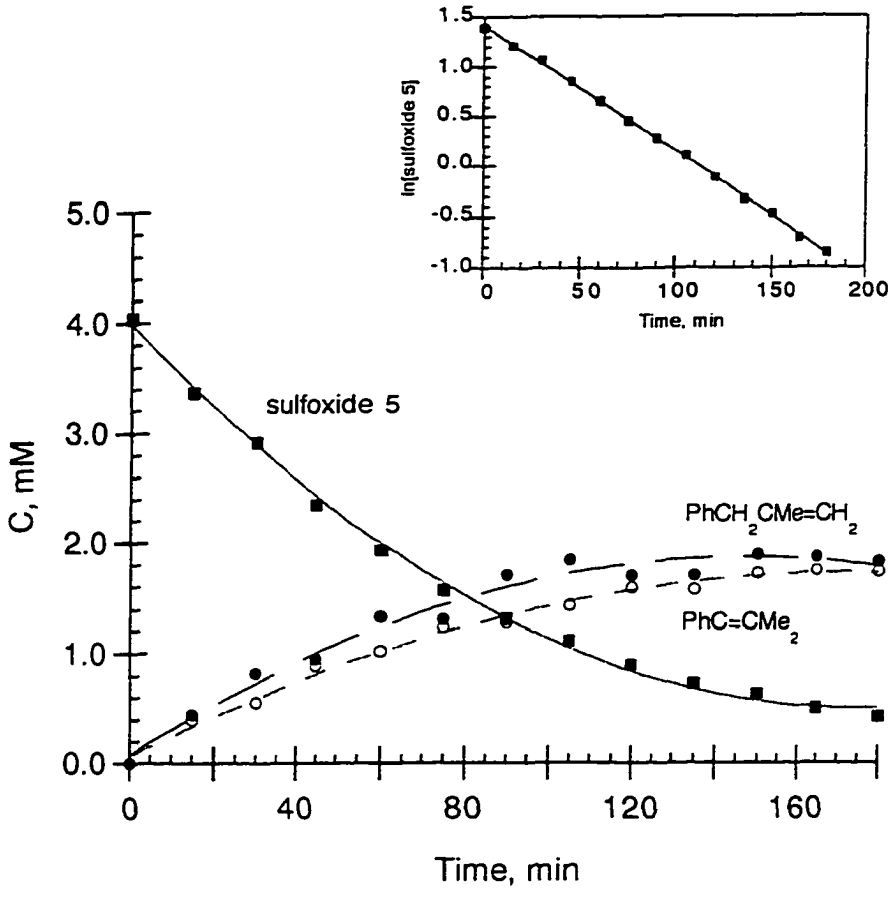


Figure 8. The thermolysis of **5** in methylcyclohexane at 86 °C. The inset shows typical first order kinetics.

Figure 11 shows the relatively linear temperature profile of the logarithm of the rate constants for sulfoxides **5** and **6**. This does not mean the absence of radical mechanisms. The reason might be the combination effect of two coexisting processes: the activation parameter decrease of the radical process (tertiary alkyl radical) and the activation parameter increase of the concerted five-membered ring elimination process (more steric hindrance). The activation parameters of the two processes are closer to each other, which results in a nearly linear rate constant profile in the limited temperature range as showing in Figure 11.

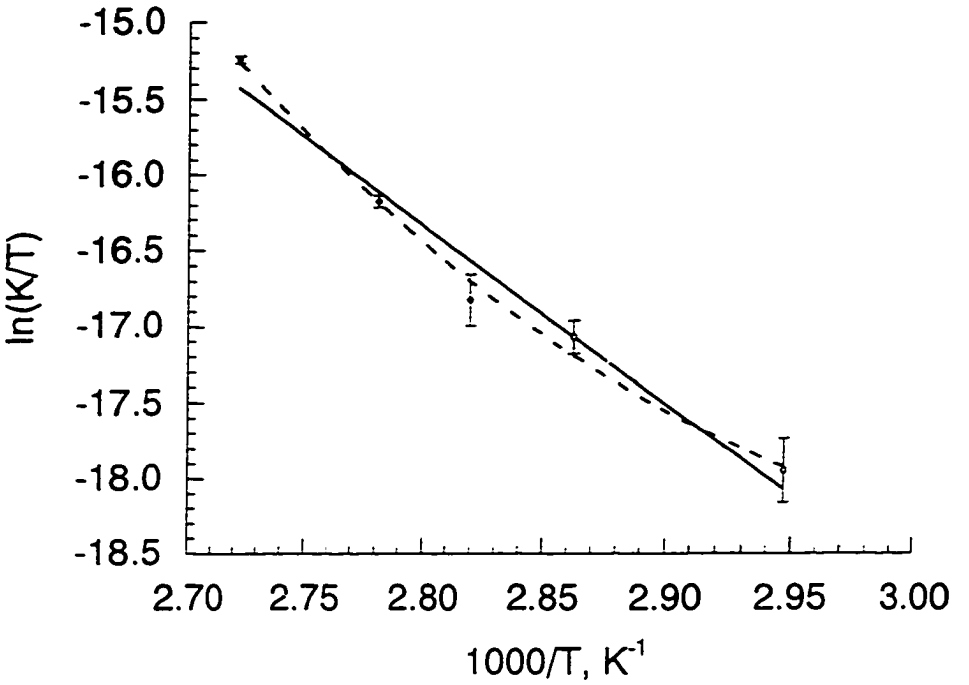


Figure 9. The temperature profile of the logarithm of the rate constant for the thermal decomposition of **4** in methylcyclohexane. The data appear to deviate from a straight line (solid).

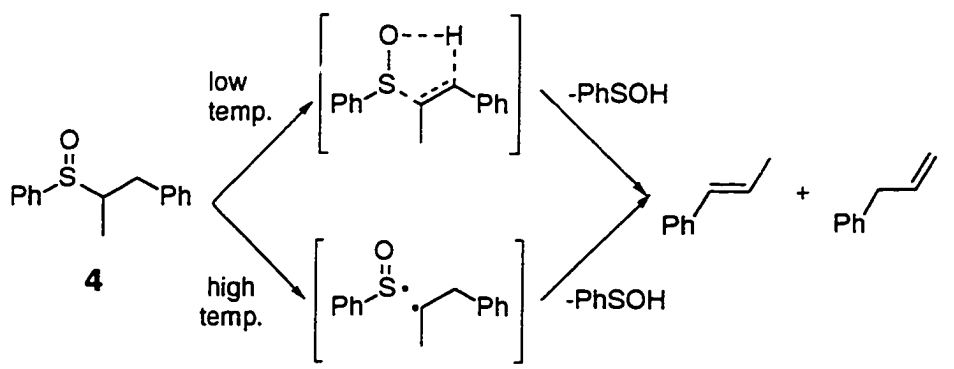


Figure 10. Concerted mechanism and radical mechanism for the thermolysis of **4**.

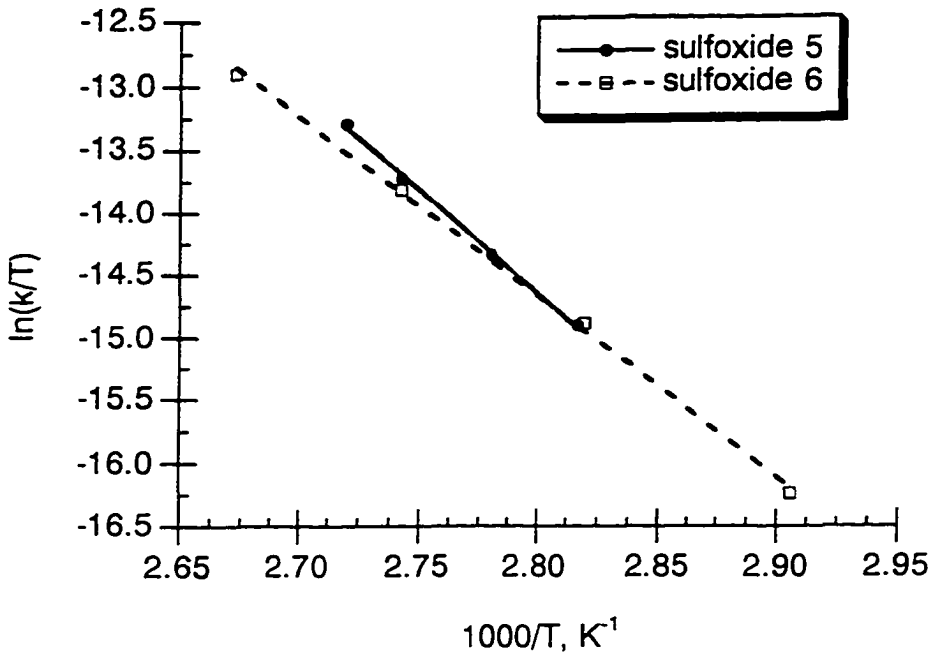


Figure 11. The temperature profile of the logarithm of the rate constants for the thermal decomposition of **5** and **6** in methylcyclohexane. The error bars ($\leq \pm 0.02$) are smaller than the size of the data markers.

Activation parameters for the decomposition of these sulfoxides were obtained by measuring the rates at several temperatures over a narrow range, and are summarized in Table 6. The positive entropy of **5** and **6** imply more radical mechanism character compared to the secondary alkyl sulfoxide **4**. This is in agreement with the higher enthalpy observed before by others.[19,31]

The lowest enthalpy and entropy of **4** among the three sulfoxides can be explained from a transition state analysis (Figure 12). We suggest that the production of **8a** comes from a transition state **4a** which is stabilized by the conjugation of the β-phenyl group. It also avoids steric hindrance by adopting the trans conformation. The **4b** transition state is also less sterically hindered, but without phenyl conjugation. By comparison, sulfoxide **5** cannot

Table 6. The activation parameters for the thermal decomposition of **4, 5** and **6** in methylcyclohexane.

	Temperature (°C)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol K)
4	66–94	23.5 ± 2.0	− 14.3 ± 6.0
8a	66–94	23.3 ± 2.0	− 15.1 ± 6.0
9a	66–94	25.5 ± 4.0	− 13.5 ± 11.6
5	80–94	32.9 ± 0.3	15.6 ± 2.5
8b	80–94	35.1 ± 1.2	19.7 ± 3.4
9b	80–94	31.7 ± 2.2	10.9 ± 6.1
6	70–100	28.5 ± 0.8	3.1 ± 2.2
8c	70–100	28.6 ± 0.9	1.3 ± 2.5
9c	70–100	28.3 ± 0.7	2.2 ± 2.1

easily achieve the analogous transition state. The transition state of **5a** (giving alkene **9b**) has the greatest steric hindrance because of the cis phenyl-methyl interaction which also interferes with conjugation of the phenyl group. Therefore, **5b** may be more favorable than **5a**. In comparison, the cis benzyl-methyl interaction in **6a** is much smaller due to the extra methylene group.

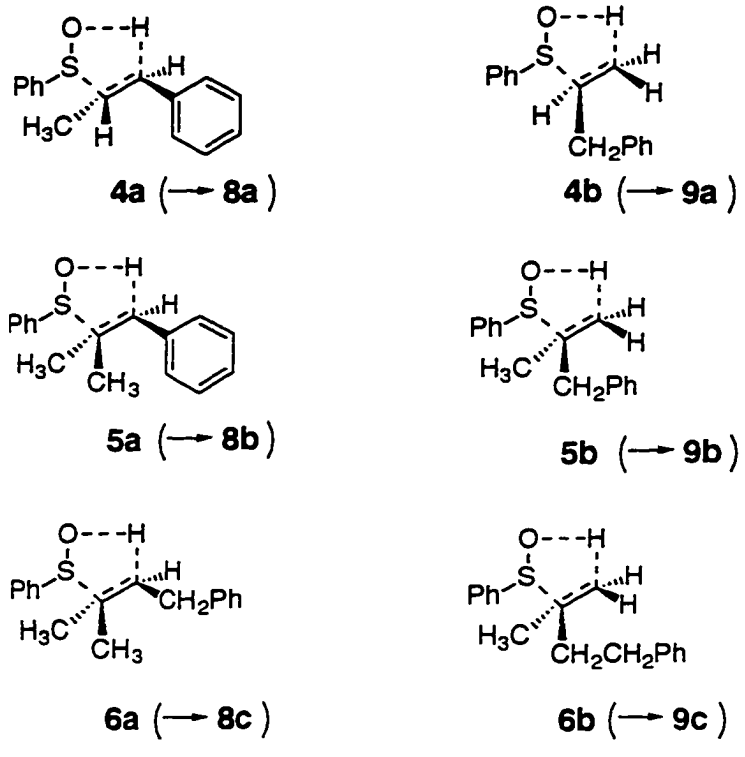


Figure 12. The transition states for *cis*-elimination of sulfoxides **4**, **5**, and **6**.

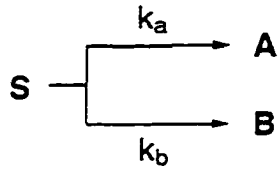
Meanwhile, in the thermolysis of sulfoxides **5** and **6**, the reaction rates that give the less stable alkenes (**9b** and **9c**) are higher than those which give the more stable alkenes (**8b** and **8c**). This supports the assumption that the relative energies of the starting state control the activation energies more than the relative energies of the products.[19]

Relative kinetics at high temperature

Gas chromatography has been used in the kinetic study of organic reactions for some time.[32] One approach is to use a specially designed pre-GC pyrolysis apparatus which can control the temperature accurately as previous described. Another approach is on column thermolysis, which uses complicated kinetic and mathematical calculations.[32] Direct injector *in situ* pyrolysis is rarely used for quantitative studies, although it has the advantage of being fast, convenient, and there is no need to modify the instruments.

Sulfoxides **4** - **6** are thermally much more reactive than **1–3**. The measurement of activation parameters by pulsed stirred-flow thermolysis was unsuccessful. Direct GC injector thermolysis was used to measure the relative activation parameters which were compared with the activation parameters obtained from solution thermolysis.

When the parallel first-order reactions yield different products as in Equation 1, the ratio of these products is proportional to their individual rate constants (Equation 2).



(1)

$$[A]/[B] = k_a/k_b \qquad (2)$$

The transition state theory treatment for each product is shown in Equation 3 and 4. From them equation 5 can be derived which related the relative activation parameters of the products with their concentration ratio. The latter can be measured from gas chromatograph.

$$\ln(k_a/T) = \ln(k_B/h) + \frac{\Delta S_a^{\ddagger}}{R} - \frac{\Delta H_a^{\ddagger}}{RT} \qquad (3)$$

$$\ln(k_b/T) = \ln(k_B/h) + \frac{\Delta S_b^{\ddagger}}{R} - \frac{\Delta H_b^{\ddagger}}{RT} \qquad (4)$$

$$\ln([A]/[B]) = \ln(k_a/k_b) = \frac{\Delta S_a^{\ddagger} - \Delta S_b^{\ddagger}}{R} - \left(\frac{\Delta H_a^{\ddagger} - \Delta H_b^{\ddagger}}{RT}\right) \qquad (5)$$

From Table 7 and Table 8, we can see that the relative activation parameters from direct thermolysis usually have higher precision than those from solution measurement. This is one of the advantages of this technique. It is more important when the two alkene isomers have very similar activation parameters, such as the **9c/8c** case where the error range in

solution thermolysis is bigger than the real value. Alkenes **9a** and **8a** have a relative good agreement between the two methods. Data for alkenes **9b** and **8b** have more deviation probably because their transition states are more sensitive to temperature change and/or solvent.

Table 7. The relative activation parameters from direct GC injector thermolysis of **4**.

A/B	T (°C)**	$\Delta(\Delta H^{\ddagger})$ (kcal/mol)**	$\Delta(\Delta S^{\ddagger})$ (cal/mol K)**
13/9a	240–300	5.3 ± 0.6	7.5 ± 1.2
13/8a(*trans*)	240–300	7.1 ± 0.4	9.1 ± 0.7
9a/8a(*trans*)	220–250	3.2 ± 0.1	4.3 ± 0.2
9a/8a(*trans*)	260–300	1.0 ± 0.1	0.06 ± 0.17
9a/8a(total)	220–250	3.0 ± 0.1	3.6 ± 0.2
9a/8a(total)	280–300	0.2 ± 0.2	− 1.7 ± 0.3
9a/8a(total)*	66–94	2.2 ± 4.9	1.6 ± 13.1
8a(*cis*)/8a(*trans*)	220–250	1.35 ± 0.06	− 0.81 ± 0.12
8a(*cis*)/8a(*trans*)	260–300	1.01 ± 0.03	− 1.45 ± 0.06

* Data from thermolysis in solution (Table 6).

** $\Delta(\Delta H^{\ddagger})$ (= $\Delta H^{\ddagger}_a - \Delta H^{\ddagger}_b$)and $\Delta(\Delta S^{\ddagger})$ (= $\Delta S^{\ddagger}_a - \Delta S^{\ddagger}_b$) are calculated assuming GC injector temperature (T) represents the thermolysis temperature.

Table 8. The relative activation parameters from direct GC injector thermolysis of **5** and **6**.

A/B	T (°C)**	$\Delta(\Delta H^{\ddagger})$ (kcal/mol)**	$\Delta(\Delta S^{\ddagger})$ (cal/mol K)**
9b/8b	220–300	0.20 ± 0.03	0.62 ± 0.06
9b/8b*	66–94	− 3.4 ± 2.5	− 8.8 ± 7.0
9c/8c	220–240	0.03 ± 0.01	− 0.68 ± 0.02
9c/8c	260–320	0.09 ± 0.01	− 0.57 ± 0.01
9c/8c*	70–100	− 0.3 ± 1.1	0.9 ± 3.3

* Data from thermolysis in solution (Table 6).

** See Table 7.

Both the production of alkane **13** and its higher $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ than the alkenes (Table 7) support the existence of a radical process along with the concerted *cis*-elimination mechanism (Figure 10). Compared to the alkene products, the relative yield of alkane **13** is very low, which suggests less contribution from the Figure 10 (b) process and/or difficulty in gas phase hydrogen abstraction by the alkyl radical. A second reason may also explain the absence of alkane products in the thermolysis of **5** and **6** (Table 8): the higher steric hindrance of the tertiary alkyl radicals. Generally, the alkene product isomers themselves have similar kinetic parameters, especially **8c** and **9c**. This is in agreement with the previous transition state analysis in the solution thermolysis.

We understand that this thermolysis is not a pure gas phase pyrolysis. It may be considered as the thermolysis of solute (sulfoxide) in a "solvent cloud". We also take caution on the temperature profile of the gas as it passes through the GC injector and the accuracy of

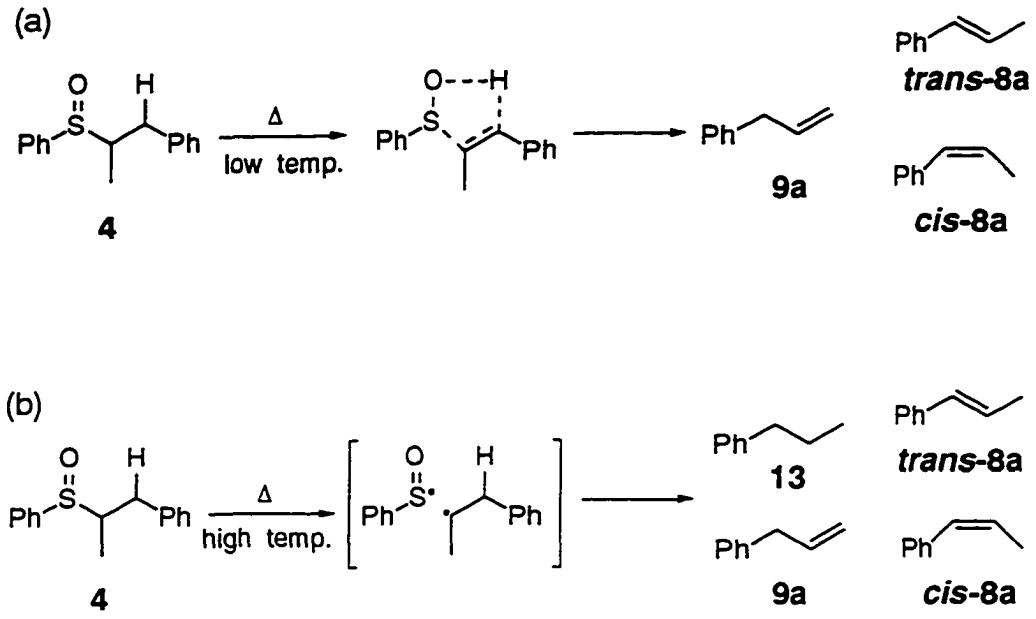


Figure 10. Concerted (a) and radical (b) thermolysis mechanisms of sulfoxide **4**.

the temperature control. However, it turns out that neither absolute temperature derivations nor relative temperature derivation cause significant deviation when reasonable values are plugged into Equation 5. A 20 °C temperature deviation causes less than a 5% deviation of the $\Delta(\Delta H^{\ddagger})$ and $\Delta(\Delta S^{\ddagger})$ values. A 50 °C temperature deviation still causes less than a 20% deviation of the $\Delta(\Delta H^{\ddagger})$ and $\Delta(\Delta S^{\ddagger})$ values. Also, a ±20% temperature deviation causes less than 20% deviation of the $\Delta(\Delta H^{\ddagger})$ and $\Delta(\Delta S^{\ddagger})$ values. $\Delta(\Delta S^{\ddagger})$ is even much less sensitive to the change of temperature than $\Delta(\Delta H^{\ddagger})$.

Summary

In this chapter, we have presented the thermolysis results of different alkyl aryl sulfoxides. The regioselectivity of the alkene products from thermolysis is controlled by the structure of the sulfoxides, which indicate a different mechanism from the photochemical process exists. High temperature thermolyses show increasing radical character as indicated by the presence of alkane products and higher activation parameters. A pulsed stirred-flow

reactor was used successfully to study the kinetics of some sulfoxides. The direct GC injector pyrolysis method bas proven to be a simple and fast way to measure the relative activation parameters of thermally unstable sulfoxides with good precision.

Experimental Section

General methods. Except as noted, HPLC grade solvents were used as received for all thermolyses. *tert*-Butyl alcohol was Fisher Scientific reagent grade and redistilled before use. A small quantity of HPLC quality water (1% by volume) was added in order to insure the *tert*-butyl alcohol did not freeze. 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. GC-MS data were obtained using a VG Magnum ion trap instrument. Other GC data, including the pyrolysis gas chromatography experimental results, 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 (5μm, 200 x 2.1mm) 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%.

3-Phenylpropylthiol. This compound was synthesized according to a literature method.[33] A mixture of 2.0 g (10 mmol) of 3-phenylpropyl bromide and 0.8 g (10.5 mmol) of thiourea in 10 ml of 95% ethanol was refluxed for 2 hours under an argon atmosphere. A solution of 0.6 g (15 mmol) of sodium hydroxide in 6 ml of water was added, and the mixture was refluxed for 2 hours. A solution of 0.7 ml of 98% sulfuric acid in 6 ml water was added and then extracted with benzene two times (2 x 15 ml). The benzene layer was collected and washed with water and dried over anhydrous sodium sulfate. After removing of the solvent, the crude product was passed through silica gel to afford 1.46 g (96% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.41 (t, J = 7.8 Hz, 1 H), 1.93–2.07 (m, 2 H), 2.54–2.62 (m, 2 H), 2.70–

2.80 (m, 2 H), 7.22–7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.1, 34.5, 35.6, 126.1, 128.5, 128.6, 141.4.

Bis(3-phenylpropyl) disulfide. This compound was synthesized by the oxidation of 3-phenylpropylthiol with iodine in near quantitative yield according to a literature method.[34] ^1H NMR ($CDCl_3$) δ 1.99–2.09 (m, 4 H), 2.70 (t, J = 7.2 Hz, 4 H), 2.75 (t, J = 7.7 Hz, 4 H), 7.19–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 30.7, 34.5, 38.2, 126.1, 128.5, 128.6, 141.4.

Methyl 3-phenylpropyl sulfoxide (1). This sulfoxide was synthesized in near quantitative yield by oxidation of the corresponding sulfide using H_2O_2 (30%) in methanol.[35] Further purification was by silica column chromatography (hexane/ethyl acetate = 75/25). ^1H NMR ($CDCl_3$) δ 2.06 (m, 2 H), 2.48 (s, 3 H), 2.54–2.70 (m, 2 H), 2.70–2.80 (m, 2 H), 7.12–7.28 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.2, 34.7, 38.6, 53.8, 126.4, 128.5, 128.6, 140.4.

The sulfide was synthesized by reaction of 3-phenylpropylthiol with methyl iodide in THF solution. 3-Phenylpropylthiol (0.61 g, 3.9 mmol) was added to a suspension of NaH in 10 ml of THF in an ice bath. Then methyl iodide (0.55 g, 3.9 mmol) in 5 ml of THF was added. The reaction was kept at room temperature for another 20 hours. 20 ml of brine was added and the mixture was extracted with methylene chloride. Pure product was obtained as a colorless oil and was purified by silica column chromatography (hexane). ^1H NMR ($CDCl_3$) δ 1.95 (tt, J = 7.8, 7.2 Hz, 2 H), 2.12 (s, 3 H), 2.53 (t, J = 7.2 Hz, 2 H), 2.75 (t, J = 7.8 Hz, 2 H), 7.15–7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.5, 30.8, 33.7, 34.9, 126.0, 128.5, 128.6, 141.7.

3-Phenylpropyl vinyl sulfoxide (2). This sulfoxide was synthesized in 90% yield by oxidation of the corresponding sulfide using H_2O_2 in methanol.[35] Further purification was done by silica column chromatography (hexane/ethyl acetate = 75/25). ^1H NMR ($CDCl_3$) δ 1.96–2.17 (m, 2 H), 2.59–2.80 (m, 4 H), 5.94 (d, J = 9.6 Hz, 1 H), 6.08 (d, J = 16.5 Hz, 1 H), 6.55 (dd, J = 16.5, 9.6 Hz, 1 H), 7.15–7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 23.2, 34.4, 52.2, 122.1, 126.2, 128.5, 128.9, 140.5, 140.6.

The sulfide was synthesized according to a literature method.[36] Vinylmagnesium bromide (13 ml, 13 mmol, 1.0 M in THF, Aldrich Chemical Co.) was added to Bis(3-phenylpropyl) disulfide (2 g, 6.6 mmol) in anhydrous ether solution at −40 °C. The reaction then was kept at room temperature for another 5 hours. The undissolved solid were filtered off and washed with hexane. The organic filtrate was collect and dried over magnesium sulfate. After removal of the solvent, the residue was distilled under vacuum (83 °C/1 mm Hg). The product was a colorless liquid obtained in 85% yield. ^{1}H NMR ($CDCl_3$) δ 1.96 (m, 2 H), 2.64–2.75 (m, 4 H), 5.08 (d, J = 16.8 Hz, 1 H), 5.17 (d, J = 10.2 Hz, 1 H), 6.33 (dd, J = 16.8, 10.2 Hz, 1 H), 7.16–7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 30.5, 30.6, 34.7, 110.7, 126.0, 128.4, 128.5, 132.2, 141.2.

The preparation of 1-methyl-2-phenylethyl phenyl sulfoxide (**4**), 1,1-dimethyl-2-phenyl phenyl sulfoxide (**5**), and 1,1-dimethyl-3-phenylpropyl phenyl sulfoxide (**6**) have been described before.[21]

Product identifications. Product identification was based on comparison with genuine samples in chromatographic behavior. HPLC-derived UV spectra were obtained and compared. Once products were established, comparison of retention times for experimental and genuine samples were reverified for any change of chromatographic conditions. Some of the alkane and alkene products were also identified by GC-MS.

Thermolysis. Unless otherwise indicated, thermolyses of sulfoxides in solution were carried out using an oil bath. A Barnant RTD temperature controller was used to keep the temperature within ± 0.5 °C. In a three neck flask equipped with condenser and thermometer, A 10 ml solution of the sulfoxide (3–4 mM) containing 1-phenylundecane (Aldrich Chemical Co., 99%) as an internal standard was heated at a certain temperature under an argon atmosphere. 5μl of samples were taken out at several time intervals and monitored by HPLC. The rates of the reactions were found to fit nicely to a first-order equation and the rate constants were calculated by a least-squares method.

GC pyrolysis was performed by injecting the same sulfoxide solutions into the GC injection port at different temperatures.

Neat thermolysis experiments were performed on the Thomas-Hoover capillary melting point apparatus. Neat sulfoxides were packed into a capillary. The decomposed sample was extracted with hexane. Alkene products were separated from other polar compounds by a silica mini-column and then measured on GC.

Pulsed stirred-flow thermolysis experiments were performed on a modified Varian 6000 Gas Chromatograph using a J&W Scientific DB-5 megabore column.[36] The helium flow rate was 20 ml/min, pressure 23 psi. An auto temperature controller was used to keep the thermal reactor furnace temperature within ± 0.5 °C. 2 μl of sulfoxide solution (~ 10 mM) in acetonitrile was injected each time. The data were processed by a microcomputer.[37]

Acknowledgment. We gratefully acknowledge financial support from the NSF (CHE 94-12964), the Petroleum Research Foundation, and the Research Corporation. Y.G. thanks the Dow Chemical Fellowship and Nelson Chemistry Scholarship at Iowa State University. The authors also express their gratitude to Dr. Sina Ijadi-Maghsoodi and Mr. Nathan Classen of Dr. Thomas Barton's group at Iowa State University for using their stirred-flowed flash thermolysis instrument and their technical assistance.

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GENERAL CONCLUSIONS

In summary, the following conclusions can be drawn from the study described in this thesis.

1. α-Cleavage as the main photochemical process for acyclic alkyl aryl sulfoxides is supported from both steady state and laser flash photolysis study. The excited sulfinyl-alkyl radical pair formed from homolysis is mainly singlet state in most cases.

2. The efficiency of photodegradation or photostability of sulfoxides is correlated to the stability of the radical pair produced by homolysis.

3. Sulfenic esters are important intermediates in the photolysis of sulfoxides, but are susceptible to secondary photolysis.

4. There may exist two mechanisms for the photo-racemization of chiral sulfoxides depending on their structures which may coincide with their thermal chemistry.

5. Intramolecular hydrogen abstraction process in acyclic sulfoxides is very inefficient or does not exist.

6. The differences in both the regioselectivity of the alkene products and the activation parameters implies two different mechanisms for their thermal and photochemical elimination processes.

APPENDIX: PHOTOCHEMISTRY INSTRUMENTATION

Low-pressure Mercury Lamps

These lamps are used in the Rayonet Photochemical Mini-Reactor (Model RMR-600) manufactured by The Southern New England Ultraviolet Company. The low-pressure lamp consists of a quartz tube 11.5 cm long and about 1.5 cm in diameter containing a droplet of mercury and a few millimeters pressure of inert gas to facilitate starting. They emit almost entirely at 253.7 nm as showed in Figure 1. Each lamp is about 8 watts of 254 nm UV light. The 300 nm "sunlight" UV lamp is identical to the 254 nm lamp except the inner wall is coated with a layer of phosphor material, which has a spectral energy distribution as showed in Figure 2. Each lamp has an output of about 3.9 watts about 300 nm range. A cooling fan was installed to keep the system at room temperature.

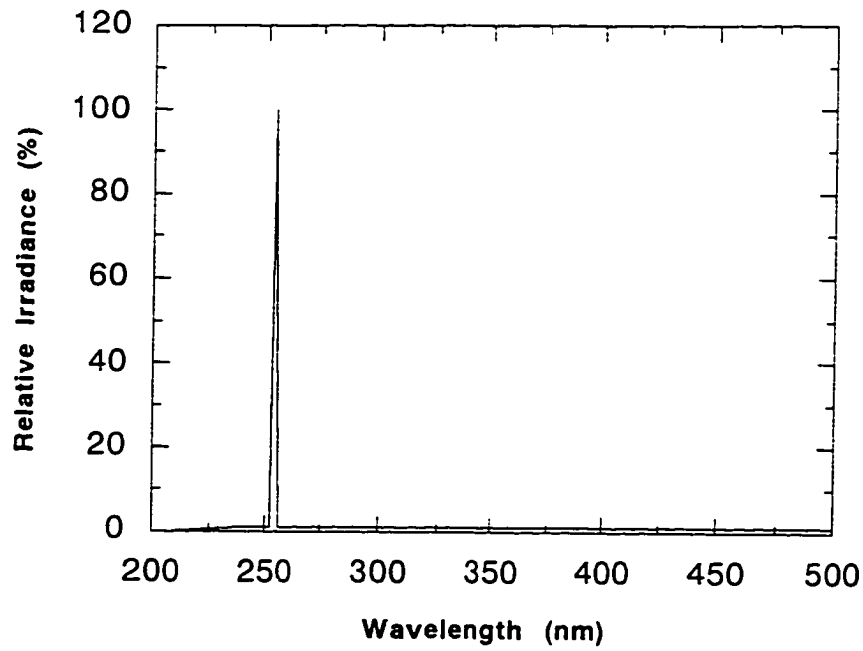


Figure 1. Spectral energy distribution curve for Rayonet RMR-1849/2537 A° lamp. Reproduced with permission of The Southern New England Ultraviolet Co., Hamden, CT.

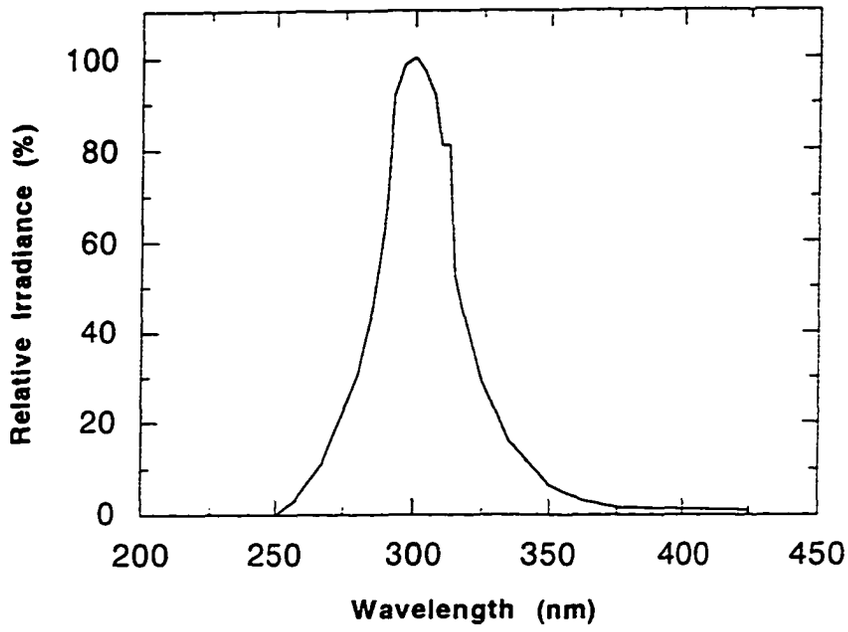


Figure 2. Spectral energy distribution curve for Rayonet RMR-300 A° lamp. Reproduced with permission of The Southern New England Ultraviolet Co., Hamden, CT.

Xenon Arc Lamps

This lamp is used in the LPS-220 monochromator system (Figure 3) manufactured by Photon Technology International (PTI). The xenon lamps operate at high pressure (about 20 atmosphere) with short arc configurations and use a DC power supply for stable operation. Lamp output consists of a smooth continuum, with a weak superposition of lines in the visible, and with strong lines observable in the near IR. Water cooling is needed to remove associated heat. The relative irradiance decreases near linearly as the wavelength decreases at 200-400 nm region. The lamp used in this thesis has a rated current of 7.5 A and output of about 150 watts. The irradiation wavelength can be adjusted to a narrow region by using a

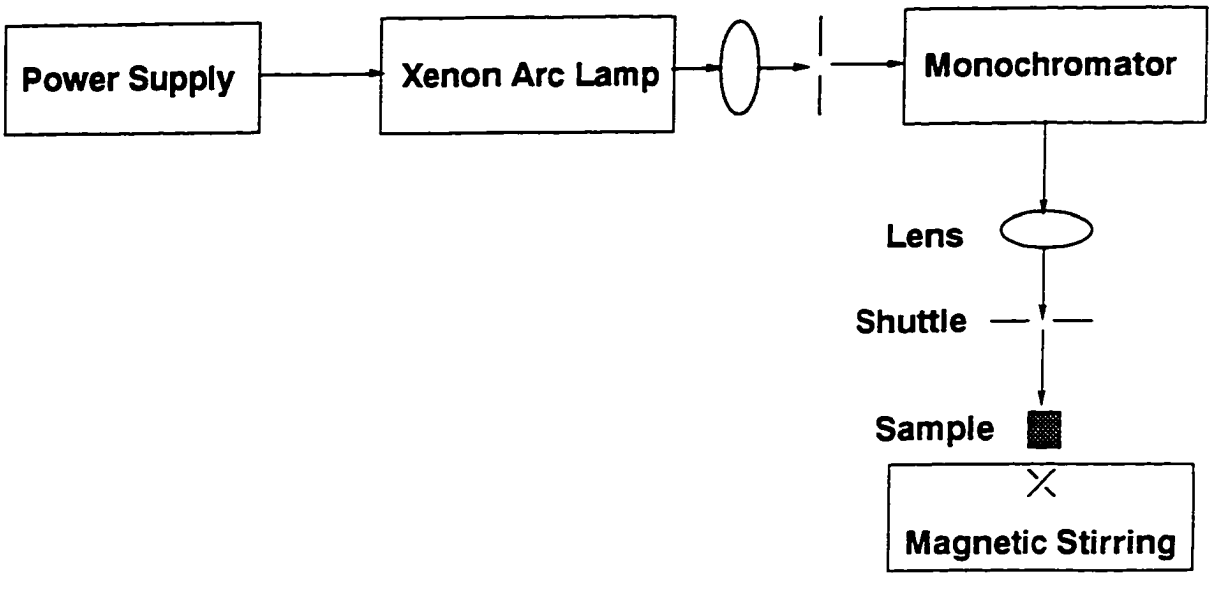


Figure 3. Diagram of a LPS-220 monochromator photolysis system

monochromator, which make this system especially useful for the accurate measurement of photolysis quantum yields in solution. However, only tens of milliwatts are finally sent to the sample after passing the monochromator, slits and several lenses.

Laser Flash Photolysis

Time-resolved laser flash spectrophotometry is very useful for the study of short-lived radical species, such as the radicals proposed in sulfoxide photochemistry. In order to achieve this object, a high energy exciting light like a laser must be used to produce a detectable transient concentration (ΔO.D. $\geq 10^{-3}$). Also the duration of the excitation must be short compared to the transient lifetime. A general laser flash photolysis setup is shown in Figure 4. The laser pulse excites the sample in the quartz cell on one side, whereas the analyzing beam crosses the cell in a perpendicular direction. In order to produce a good signal/noise ratio, the absorbed light must be the highest possible, because of the small

transient concentration. An intense xenon arc lamp is often used as the analyzing light beam for short-lived transients and was triggered by the laser control unit. A monochromator and a photomultiplier are used to record transient absorptions at various wavelengths which are normalized to a constant laser pulse dose and digitized for computerized kinetic analysis.

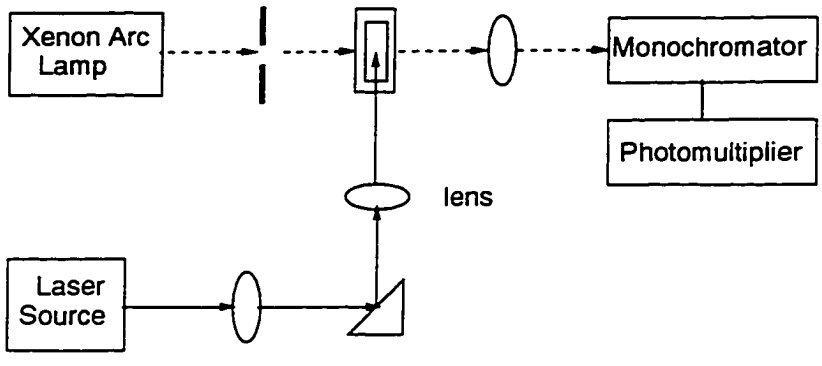


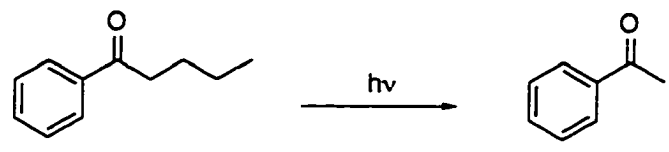
Figure 4. Simplified diagram of a laser flash photolysis equipment.

Chemical Actinometry and Quantum Yield

The quantum yield (Φ) is the efficiency measurement of a photochemical process. It is equal to the number of molecules of photoproduct formed (or starting material disappearance) per photon of light absorbed. Quantum yield can also be viewed as the probability that the initially generated electronically excited state will yield the given photoproduct. The quantum yield for a photochemical reaction depends on the relative rates of the various competing processes occurring from the electronically excited states. It may not be a good measurement of the absolute photoreactivity of excited states because of the partitioning that leads back to starting material. Determination of photochemical quantum yields requires knowledge of the number of photons absorbed during a particular experiment. An actinometer is a chemical system or a physical device by which the number of photons in a beam can be determined integrally or per unit time. In a chemical actinometer photochemical conversion is directly related to the number of photons absorbed. In 1989

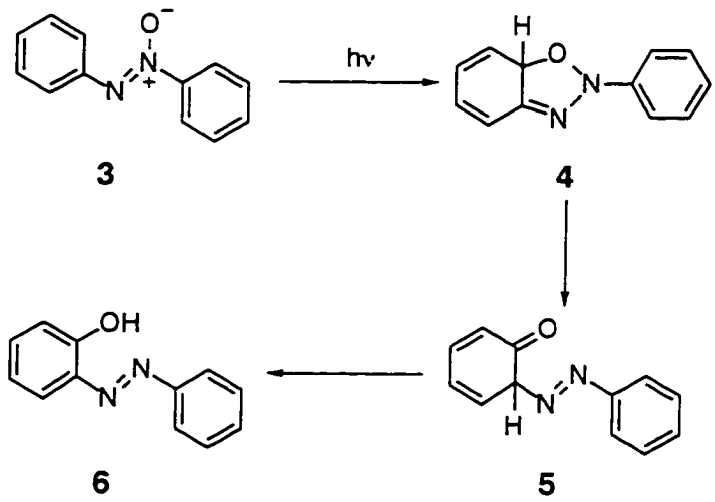
IUPAC published a detailed report on chemical actinometry, which includes a list of total 67 photochemical systems (7 in solid phase, 19 in gas phase, and 41 in liquid phase).[1]

Two chemical actinometers were used in the research described in this thesis. The first is the valerophenone **1** Norrish type II photoelimination system.[2] Quantum yields of acetophenone (**2**) formation are solvent dependent, which range from 0.38 in hydrocarbon solvents to 0.90 in *tert*-butyl alcohol under the irradiation of 313 nm at 25 °C.



1 **2**

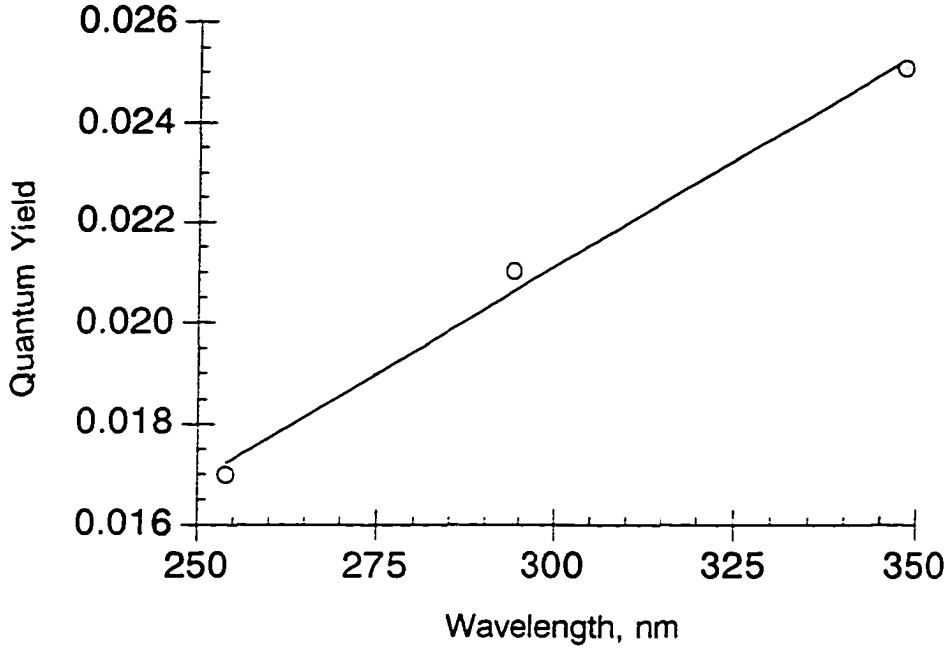
The other chemical actinometer used more extensively in our research is the photorearrangement of azoxybenzene (**3**) to 2-hydroxyazobenzene (**6**).[3] Azoxybenzene can be easily prepared by reduction of nitrobenzene in methanol and purified by recrystallization from alcohol.[4]



3 **4** **6** **5**

In ethanolic solution, the intramolecular photorearrangement of azoxybenzene occurs with a quantum yield about 0.02 over the range 250–350 nm. The reaction, which is almost independent of temperature (22–45 °C) and of concentration (0.5–5.0 mg/ml), is

conveniently monitored by measuring the absorbance of the product anion in alkaline solution. Also the quantum yield and irradiation wavelength has a near linear relationship, which allows the measurement of quantum yield at almost any wavelength in the 250–350 nm region (Figure 5).



Quantum Yield = 0.0042 + 8.45 x 10^{-5} x Wavelength (nm)

Figure 5. Quantum yield and wavelength correlation of azoxybenzene actinometer.

Thus, under the conditions when all incident light is absorbed by both actinometer and test solution, by definition:

$\Phi_{actinometer}$ = (Moles of product from actinometer)/(Moles of photons absorbed)

The number of moles of product from actinometer molecule decomposition per unit time is $V_{actinometer}\Delta C/\Delta t$, where $\Delta C/\Delta t$ is the slope of the plot of concentration C as a function of irradiation time, e.g., the rate of production of acetophenone or 2-

hydroxyazobenzene determined by chromatographic or spectroscopic instruments. Hence, the absorbed light flux (I) in units of (mole/unit time) is:

$$I = (V_{actinometer}\Delta C/\Delta t)/\Phi_{actinometer}$$

When both actinometer and test sample are under the same photolysis conditions (same light flux), the quantum yield of test sample can be calculated by the following equation:

$$\Phi_{sample} = (V_{sample}\Delta C'/\Delta t)/I$$

$\Delta C'/\Delta t$ is the decomposition rate of test sample or production rate of photolysis products, which are usually determined by analytical instrumental methods.

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ACKNOWLEDGEMENTS

I would like to thank my major professor, William S. Jenks, for his encouragement and helpful guidance and discussions - from chemistry to English. I would also like to thank other members of my Program of Study Committee, for their time and participation in my degree program: Professors Glen A. Russell, Professor Richard C. Larock, Professor James Espenson, Professor Joshua U. Otaigbe, and Dr. Agustin Kintanar.

I owe special thanks to Professor William S. Jenks and Professor Richard C. Larock for their critical and thorough review of my manuscript and for providing me with very valuable suggestions and corrections.

Thanks are extended to all the members of the Jenks group for their friendship and the time shared in the lab. I really appreciate Dan Gregory, Jerry Cubbage, Woojae Lee, and Troy Tetzlaff for helping me editing the drafts my thesis.

I would like to thank other research groups and persons of the Chemistry Department at Iowa State for their loans or gifts of chemicals and equipments for my research: Russell group, Larock group, Espenson group, Barton group, Kraus group, Trahanovsky group, Dr. John Hayes, and Allen Clague.

I also gratefully thank the support of the Dow Chemical Fellowship and Nelson Chemistry Scholarship of Iowa State University.

I am extremely grateful to my parents and parents-in-laws for their loving support. I thank them for their understanding during all of the times when I could not be with them and for their steady love that supports me.

Finally, I would like to thank my wife Fan for her love, support, and understanding. I owe her in ways that are too numerous to mention. This dissertation would not have been possible without her.