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Sulfoxides of thiophene and dibenzothiophene: a mechanistic study of photochemical deoxygenation

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Sulfoxides of thiophene and dibenzothiophene: A mechanistic study of photochemical deoxygenation

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This is to certify that the doctoral dissertation of

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Signature was redacted for privacy.

Major Professor

Signature was redacted for privacy.

For the Major Program

To

Gargi

My wife

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Abstract

Dibenzothiophene oxide (**DBTO**) produces dibenzothiophene (**DBT**) as the only detectable photoproduct. Although the chemical yield of deoxygenation is very high, the quantum yield is relatively low. Indirect evidence also indicates formation of $O(^3P)$ as the other photoproduct. The quantum yield of deoxygenation increases in the presence of oxygen trapping solvents. From these results, a mechanism for the deoxygenation was proposed which indicates a unimolecular S-O bond scission and a S-O bond stretch coupled to intersystem crossing.

Heavy atom substituted **DBTO**s show high efficiency of phosphorescence but a moderate increase in the deoxygenation quantum yield. However, the order of increase in both phosphorescence and deoxygenation quantum yields are in accord with the heavy atom effect. 4-Iodo **DBTO** also undergoes deiodination via a secondary photolysis.

Alkenyl and sulfenyl groups were appended to the 4-position of **DBTO** to check whether they increase the efficiency of the deoxygenation. Photolysis of these substituted **DBTO**s showed increase in the quantum yield and for substituted **DBTO**s detectable amount of intramolecular trapped products were also formed. The quantum yield of deoxygenation was less solvent dependent for this series of **DBTO**s. However, in cyclohexene the quantum yield was similar to that observed for **DBTO**, and no intramolecular trapped products were found. This could be due to the fact that cyclohexene is a better trapping agent than the appended alkenyl and sulfenyl groups, and due to its presence in a large excess compared to the trapping group concentration. However, detection of intramolecular trapped products suggests that solvent effects observed in previous studies of **DBTO** derive at least mainly

from the reactivity between the oxidizing species that is released – presumably $O(^3P)$ – and the solvent, rather than from other macroscopic solvent parameters.

Unlike **DBTO**, mechanistic studies for the deoxygenation of thiophene oxide (**TO**) are little known. The S-O bond breaking energy in **TO** is about 15 kcal/mol less than that of **DBTO**, whereas its first excited singlet state has almost the same energy as **DBTO**. Stable substituted **TO** derivatives were prepared hoping that they would produce $O(^3P)$ with high efficiency. Results obtained for 2,5-bis(trimethylsilyl) **TO** are promising. The quantum yield of deoxygenation in benzene was about 14 times higher than for **DBTO**. However, only about half of the disappearance was accounted for by the appearance of the corresponding thiophene. Other thiophene oxides, which were photolyzed either produced furan or other unknown products. It is possible that there is an analogy between the deoxygenation mechanism of **DBTO** and **TO** but it is too early to speculate that. At least, it is fair to say that the photochemistry of **TO** derivatives is more complicated and more substituent dependent than that of **DBTO** derivatives.

CHAPTER 1

PHOTOCHEMISTRY AND PHOTOPHYSICS OF AROMATIC SULFOXIDES: A GENERAL REVIEW

1.1 Dissertation organization

This dissertation contains five chapters. Chapter 1 is a general review of the photochemistry of dibenzothiophene (**DBTO**s) and thiophene oxides (**TO**s). This chapter is composed of mainly the literature reviews available for the photochemical processes of the previously mentioned compounds. Chapter 2 and Chapter 3 are based on two independent published papers. Chapter 4 is the basis of another publication.

Chapter 2 discusses the photochemistry and photophysics of heavy atom substituted **DBTO**s. In Chapter 3, the photochemical deoxygenation of **DBTO**s with O atom accepting substituents is discussed. In Chapter 4, the photochemistry of various substituted stable thiophene oxides is discussed. Chapter 5 contains general conclusions and a summary of previous chapters.

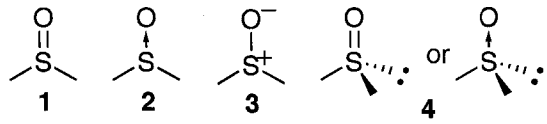
While the majority of the work described here was carried out by the author, there were contributions from another group member. Some of the experiments discussed in Chapter 4 were performed by Melanie Heying.

1.2 Objectives

The overall goal of this dissertation is to develop a better understanding of the photochemical processes of dibenzothiophene and thiophene oxides. The contents of the next two chapters are related and discuss the photochemical deoxygenation process of the substituted aromatic sulfoxide, **DBTO**. The fourth chapter is about another aromatic sulfoxide, thiophene oxide, whose photochemistry is relatively unexplored compared to the **DBTO** derivatives.

1.3 Fundamental properties of sulfoxide groups

Superficially, the sulfoxide or sulfinyl functional group has many similarities to carbonyl functional groups. Both of the functional groups have polar bonds where oxygen is the more electronegative atom. Both the functional groups show α-cleavage as one of their main photochemical reactions, and both groups tend to stabilize α-carbanions. Despite these similarities, there is a fundamental difference between them. In carbonyl groups, the carbon atom is sp^2 hybridized, whereas in sulfoxides the sulfur atom is approximately sp^3 hybridized. Hence, unlike the carbonyl groups no true π-bond can be found in the sulfoxide groups. At the same time, the sulfoxide bond cannot be represented by a simple single bond. Because of the complexity of the sulfoxide bond there is no universally accepted simple orbital description established for this bond. Sulfoxides are commonly illustrated with a simple double bond (**1**). Alternative, and perhaps more correct representations include an ylide **2**, a structure with a charge-separated single bond (**3**), or one with a stereochemical representation (**4**).



The ylide form **3**, where an electron pair is localized on the oxygen atom, represents many aspects of the sulfoxide reasonably accurately. However, with the aid of computation it is now established that sulfur atoms do not have three equivalent sp^3 hybridized bonds and a lone pair. The CSC bond angle of DMSO was calculated to be around 95°, which is considerably smaller than the ideal sp^3 hybridized angle. Structure **3** is used in literature mostly by computational chemists. Structure **4** is a useful representation of chiral sulfoxides. All of these structures are well accepted and represent the same molecule. For consistency structure **2** will be used in this dissertation.

Organic sulfur compounds can have various oxidation states; among them sulfoxides are an intermediate case. Sulfoxides can be readily oxidized to sulfones or reduced to sulfides. Several different, but related, sulfur functional groups and their nomenclatures are listed in Figure 1.

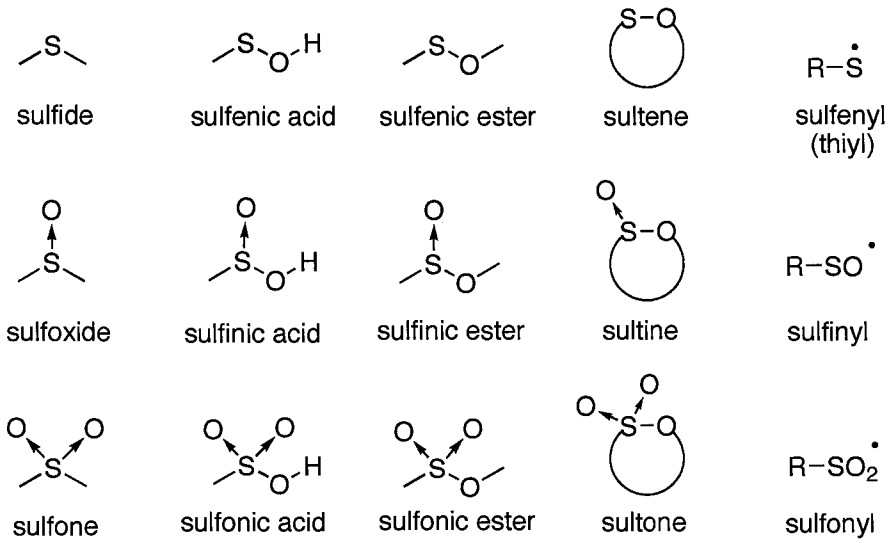


Figure 1. Nomenclature of common sulfur containing functional groups

The main purpose of this research is to characterize the photo-deoxygenation mechanism of aromatic sulfoxides. The aromatic sulfoxides that will be discussed in the next three chapters are derivatives of dibenzothiophene-5-oxide (**DBTO**, **5**) and thiophene oxide (**TO**, **6**).

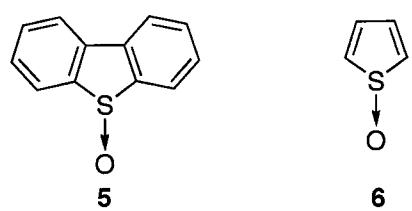


Figure 2. Structure of **DBTO** and **TO**

1.4 A review of photochemistry of sulfoxides

The next few chapters will mainly discuss the photochemical deoxygenation and photophysics of some aromatic sulfoxides. Although the sulfoxides designed and investigated for the purpose of this work showed deoxygenation as their only photochemical reaction, deoxygenation is only a minor process among most of the sulfoxides. There are fundamentally four different unimolecular chemical changes a sulfoxide can undergo under photochemical conditions; these include α-cleavage, hydrogen abstraction, deoxygenation and stereomutation. The deoxygenation process will be discussed in detail later in this chapter since it is the main reaction investigated in this research, but at the same time it is worthwhile to know about other important photochemical reactions of sulfoxides. The next few sections will cover the four main photochemical processes of sulfoxides.

1.4.1 α-Cleavage

The most common photochemical reaction of sulfoxides is α-cleavage. As mentioned above, this reaction takes place in a similar fashion to carbonyl photochemistry. Under photochemical conditions, sulfoxides undergo homolytic cleavage between the sulfur and the carbon atoms to form a carbon centered radical and a sulfinyl radical **7**, which has two important resonance structures (Figure 3). These two radicals can recombine to form a sulfenic ester or sulfoxide. Dimerization of the sulfinyl radical eventually leads to a thiosulfonate. Radical **7** also can lose SO form another carbon centered radical, though this process is limited to occasions where there is an extra driving force, such as aromatization. When the sulfoxide is cyclic, a diradical is formed instead of a radical pair.

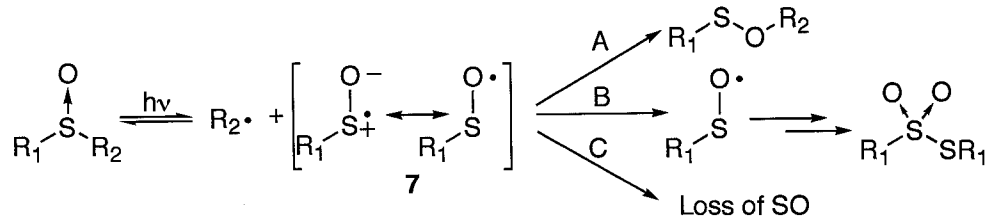


Figure 3. α-Cleavage of sulfoxides

1.4.1.1 α-Cleavage of dialkyl sulfoxides

Direct and sensitized photolysis of dimethyl sulfoxide (DMSO) was investigated in detail by Gollnick and Stracke.[1-3] Excited singlet DMSO was postulated to undergo three different chemical changes (Figure 4). No sensitized reaction was observed for DMSO; however, the authors used only ketones as sensitizers, and ketones have lower triplet energies than DMSO.

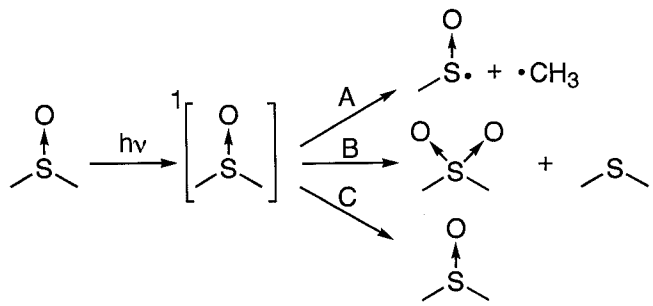


Figure 4. Photochemical reaction of DMSO

In path A, the excited sulfoxide undergoes α-cleavage to form a methanesulfinyl radical and a methyl radical. Path B represents a disproportionation reaction, which forms sulfide and sulfone from two molecules of sulfoxide. Path C is simply non-radiative decay to the ground state sulfoxide. Path C was observed only when the DMSO concentration was

high. The quantum yield of α-cleavage was independent of solvents and was measured to be 0.14. Isotope labeling experiments revealed that there were other important pathways involved in the reaction, in addition to the simple α-cleavage mechanism. When DMSO was photolyzed in a deuterated alcohol, the molar ratio of the formation of CH_4 to CH_3D varies from 1:1 in CH_3OD, to 3:1 in C_2H_5OD, to 11:1 in $(CH_3)_2CHOD$, which proved the existence of a non-radical mechanism for the formation of methane. Also, the photolysis of d_6-DMSO in non-deuterated solvents produced CD_3H exclusively, which cannot be explained by the usual disproportionation reaction of DMSO. There was also other evidence, including the effect of pH on the quantum yield, the lack of ^{18}O exchange, and the pattern of the H/D ratios, which points towards an electron transfer mechanism from the methanesulfinyl radical to the methyl radical (Figure 5).

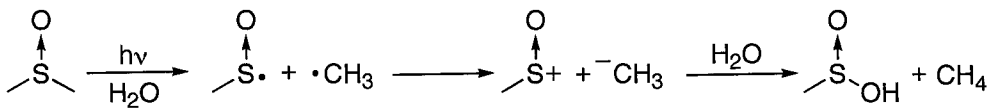


Figure 5. α-Cleavage followed by electron transfer

Weiner and coworker reported laser induced fluorescence (LIF) studies of DMSO at 193 nm.[4] Their studies showed the formation of a methyl radical and SO, but no methylsulfinyl radical was found. Later, molecular beam time-of-flight (TOF) mass spectrometry experiments by Ng *et al.* detected both the methanesulfinyl and the methyl radicals.[5] Sulfur monoxide was also detected, which originated mainly from a secondary decomposition of methylsulfinyl radical. The quantum yield for the formation of the methyl radical was 1.53. No sulfur oxygen bond cleavage was observed.

There are two different mechanisms by which DMSO decomposes photochemically. The first is single step decomposition, and the second is a stepwise mechanism (Figure 6). Recently Bañares *et al.* reported the UV photodissociation dynamics of d_6-DMSO using resonance enhanced multiphoton ionization (REMPI) and time-of-flight mass spectrometry (TOFMS).[6] The results from their experiments point to a stepwise mechanism. Three channels were identified for the formation of the CD_3 radical. The primary channel proceeds via an internal conversion to the ground state, followed by a unimolecular decomposition to the internally hot $CD_3SO(*)$ fragment. This fragment subsequently decomposes over an exit barrier (45 ± 2 kJ/mol) to produce the CD_3 radical and SO.

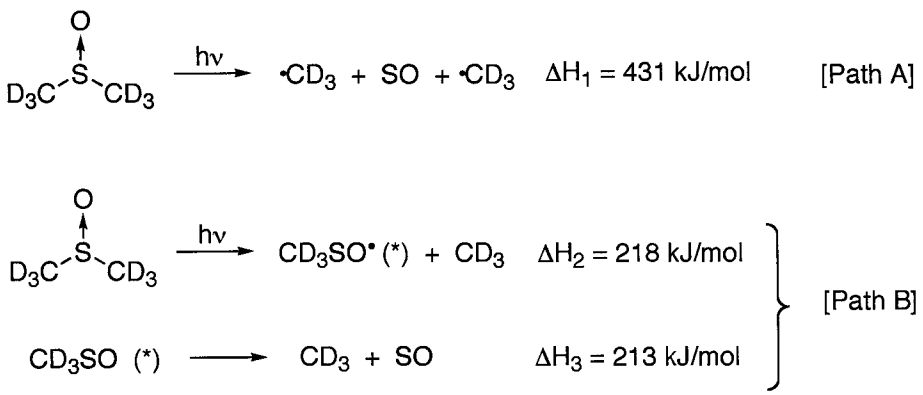


Figure 6. Photochemical decomposition of d_6-DMSO

Shelton and Davis reported the solution phase photochemistry of dialkyl sulfoxides, such as di-*tert*-butyl sulfoxide and diisopropyl sulfoxide.[7] Although several products formed in the photolysis could be explained by α-cleavage, the main product in some solvents was the corresponding sulfide. For example, the photolysis of di-*tert*-butyl sulfoxide produced

tert-butanol, di-*tert*-butyl disulfide and a small amount of acetone along with the main product di-*tert*-butyl sulfide.

1.4.1.2 α-Cleavage of benzylic sulfoxides

Dibenzyl sulfoxide, although a dialkyl sulfoxide, shows photochemistry that is closely related to the diaryl and the alkyl aryl sulfoxides. The main chromophore in the dibenzyl sulfoxide is the benzyl system rather than the sulfinyl system, and the main photochemical reaction probably derives from the benzyl chromophores. The α-cleavage reaction produces the relatively stable benzenesulfinyl radical **8** and benzyl radical **9** (Figure 6). Sato and coworkers reported the photolysis results of dibenzyl sulfoxides.[8,9] The main photoproducts were benzaldehyde **13** and benzyl mercaptan, the latter of which was isolated as dibenzyl disulfide **14**. Formation of these two products along with a minor product, benzyl alcohol **15**, can be explained by the mechanism outlined below. Dibenzyl sulfoxide produces an intermediate **10**, which upon further photolysis forms product **13**, **14** and **15**. Another minor photoproduct, bibenzyl **16**, probably forms by the dimerization of benzyl radical **9**.

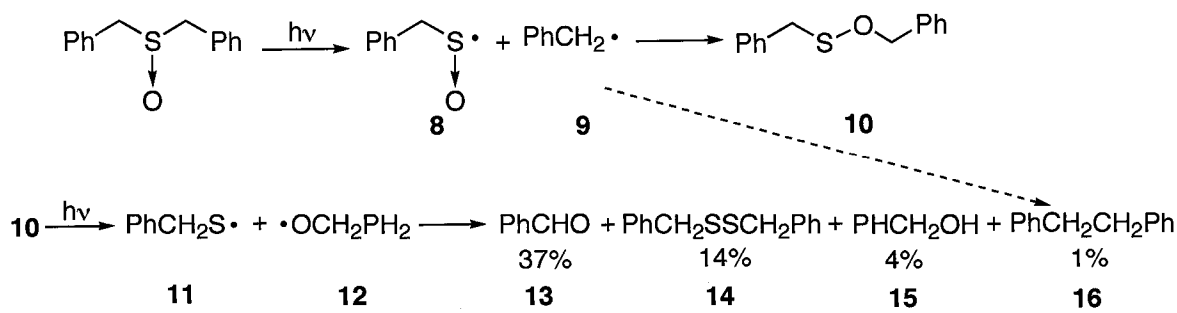


Figure 7. Photochemical cleavage of dibenzyl sulfoxide

Photolysis of phenyl benzyl sulfoxide was studied in detail by Guo and Jenks in the mid 1990s.[10] The photolysis of sulfoxide **17** using 254 nm light produced radical pair **18** and **9** by an α-cleavage reaction. The cleavage pattern is driven by the product stability. Since the benzyl radical is more stable than the phenyl radical, the other cleavage pattern forming a phenyl radical, was not observed. This radical pair forms a transient intermediate **19**, which forms another radical pair, **20** and **12**, and subsequent products via secondary photolysis. The first radical pair also gave the starting material back with racemization along with a small amount of escape products **21** and **22**. Triplet sensitization by acetone dramatically increased the percentage of escape products. From these results, it was concluded that the primary process on direct irradiation was the α-cleavage reaction of compound **17** in its singlet excited state. Also, it was evident from the product mixture that the photolysis of intermediate **19** only led to S-O homolytic bond cleavage and no O-C cleavage.

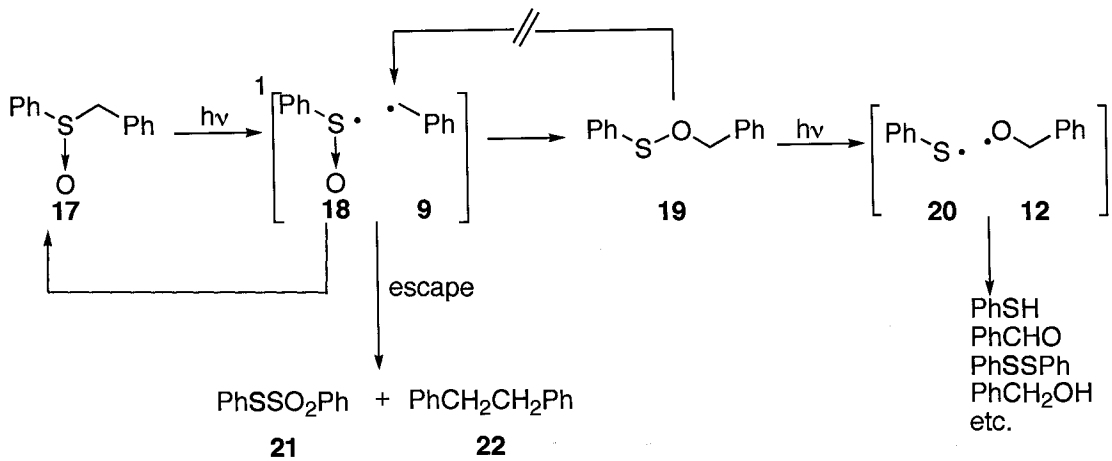
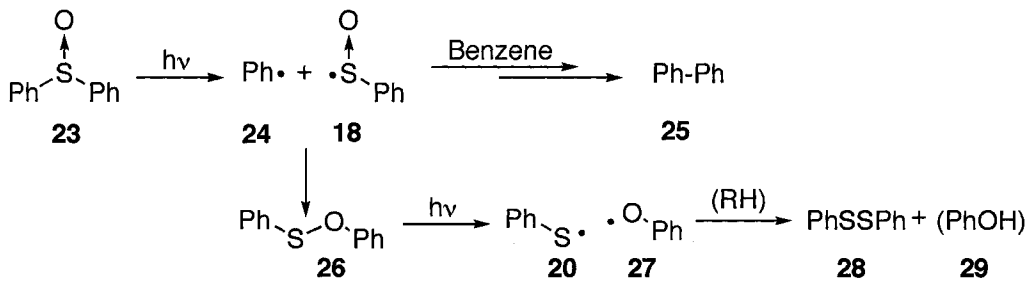


Figure 8. Mechanism for the photolysis of phenyl benzyl sulfoxide.

1.4.1.3 α-Cleavage of alkyl aryl and diaryl sulfoxides

There are several examples of photochemical reactions of various alkyl aryl and diaryl sulfoxides in the literature.[11,12] The main difference between these two sulfoxides and dialkyl sulfoxides is in their absorption properties. Alkyl aryl, and diaryl sulfoxides' absorbance spectra show a significant bathochromic shift in their UV absorption compared to their dialkyl counterpart.

Kharasch and Khodair first reported the photochemistry of diphenyl sulfoxide, the simplest possible diaryl sulfoxide.[13] Photolysis in benzene produced biphenyl **25** as the main product (53%), diphenyl sulfide (7%), and a trace amount of diphenyl disulfide **28** (Figure 8). The formation of biphenyl was explained by the reaction between photochemically generated phenyl radical and benzene solvent. The formation of **28** can be explained by the formation of phenylbenzenesulfenate **26** followed by its secondary photolysis.



23 **24** **18** **25** **26** **20** **27** **28** **29**

Figure 9. Photochemical reaction of diphenyl sulfoxide.

Nakabayashi and coworkers showed clear evidence for the combination of photochemically generated radicals and solvent.[14] When they performed the photolysis of *p*-tolyl sulfoxide **30** in pyridine as a solvent, they detected *ortho*-, *meta*-, and *para*-(*p*-tolyl) substituted pyridines **31** (Figure 10).

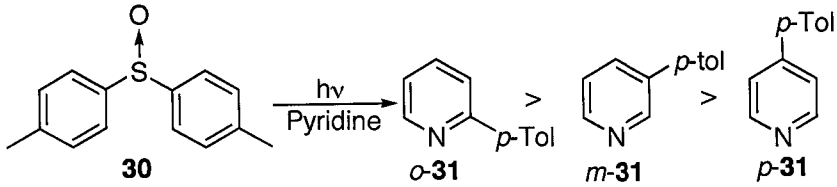


Figure 10. Photoreaction of *p*-tolyl sulfoxide in pyridine

Guo and Jenks reported the photolysis of a series of alkyl aryl sulfoxides in 1997.[15] In the proposed mechanism the initial step of the photolytic process was described as α-cleavage to form sulfinyl/alkyl radical pairs. This radical pair fragments between recombination to starting material, formation of sulfenic esters, disproportionation to an olefin and benzenesulfenic acid, and formation of typical radical escape products. It was shown that the quantum yield for conversion was dependent on the structure or the stability of the alkyl radical, with the sequence benzyl > tertiary alkyl > secondary alkyl > primary alkyl > (di)aryl. The cleavage occurred from both sides when the alkyl group was primary. On the other hand, when the alkyl group was secondary, tertiary, or benzyl, high selectivity was observed for alkyl-S cleavage. In another instance Jenks and coworkers also detected a β-naphthylsulfinyl radical in the laser flash photolysis of benzyl β-naphthyl sulfoxide.[16]

In 1997 Jenks *et al.* provided the most direct evidence for the intermediacy of the sulfinyl radical in sulfoxide photochemistry.[17] Nanosecond laser photolysis of sulfoxides **23** and **32-34** produced transient arylsulfinyl radicals, which were detected by a nanosecond transient absorption spectrometer (Figure 11). The absorption spectrum of the phenylsulfinyl radical had absorption maxima at 300 and 450 nm. The absorption spectrum was also found to be independent of the solvents. Computational studies performed by the authors indicated

that the singly occupied orbital is highly localized on the S and O atoms in a π^* configuration lying most heavily on oxygen.

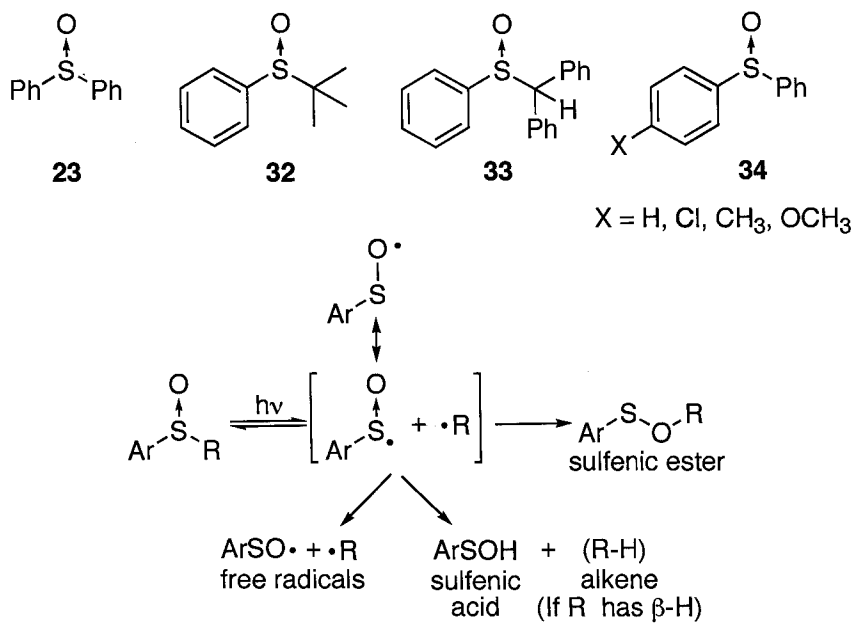


Figure 11. Photolysis of aryl alkyl and diaryl sulfoxides

1.4.1.4 SO extrusions

Photochemical extrusion of SO_2 from the sulfone group is a common reaction. Although some sulfoxides show similar reactivity, SO extrusion is not as common for sulfoxides as for sulfones. The loss of SO from the sulfinyl radical, a product of α-cleavage, was calculated to be endothermic by about 50 kcal/mol,[18] so SO extrusion is not observed at room temperature in solution.[19] The SO extrusion is most likely a stepwise reaction[11] and it only happens when there is a significant amount of positive entropy or high product stability caused by the second C-S cleavage (Figure 12).

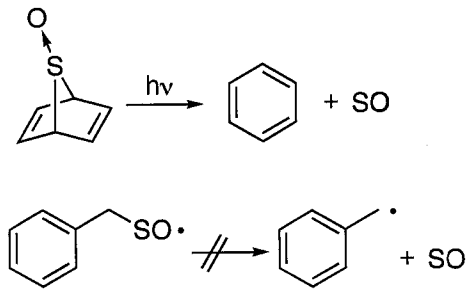


Figure 12. SO extrusion reactions

The first reported SO extrusion reaction was observed by Kellog and Prins in 1974.[20] In their report they mentioned the SO extrusion reaction of dihydrothiophene oxide systems in both photochemical and thermal conditions. The photolysis of sulfoxides **35** produced dienes **36** as mixtures of isomers (Figure 13). Since no single isomer was formed, a concerted mechanism was ruled out, and a stepwise mechanism involving α-cleavage as the first step of the reaction was adopted.

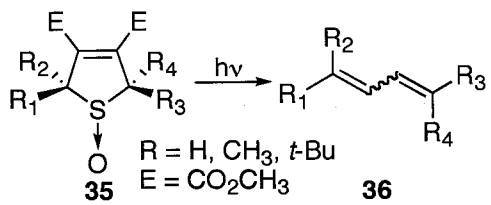


Figure 13. SO extrusion reaction of dihydrothiophene oxides

Carpino and Chen showed another example of an SO extrusion reaction where 2,3-diphenylthiirene-1-oxide **37** was photolyzed to give diphenylacetylene **38** as the only product (Figure 14).[21] On the other hand, the pyrolysis of the same compound produced benzil **39** by a mechanism which is yet to be elucidated.

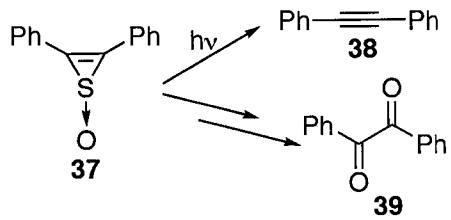


Figure 14. Photolysis and pyrolysis of diphenylthiirene-1-oxide

1.5 Hydrogen Abstraction

Hydrogen abstraction is a very common reaction of carbonyl compounds. Due to its apparent structural similarity with carbonyl compounds many photochemical reaction of sulfoxides were explained by the hydrogen abstraction mechanism. However, since we know now there is little analogy between the sulfoxide and carbonyl bonds, there is also very little evidence for the hydrogen abstraction mechanism in case of sulfoxides.[11] In fact most of the sulfoxide photolysis products formed, which were earlier thought to be formed via a hydrogen abstraction mechanism, can also be explained by the α-cleavage mechanism.

Guo and Jenks designed an experiment to elucidate the mechanism for the photodegradation of aryl alkyl sulfoxides.[10] The systems were chosen in such a way that there were provisions for β- and γ-hydrogen abstractions. Two such sulfoxides, **40** and **47**, were photolyzed to check whether hydrogen abstraction products were being formed or not (Figure 15). No products, which could be formed only by the hydrogen abstraction mechanism were isolated. From these experiments it is evident that although the hydrogen abstraction mechanism cannot be completely ruled out, there is very little evidence in favor of it.

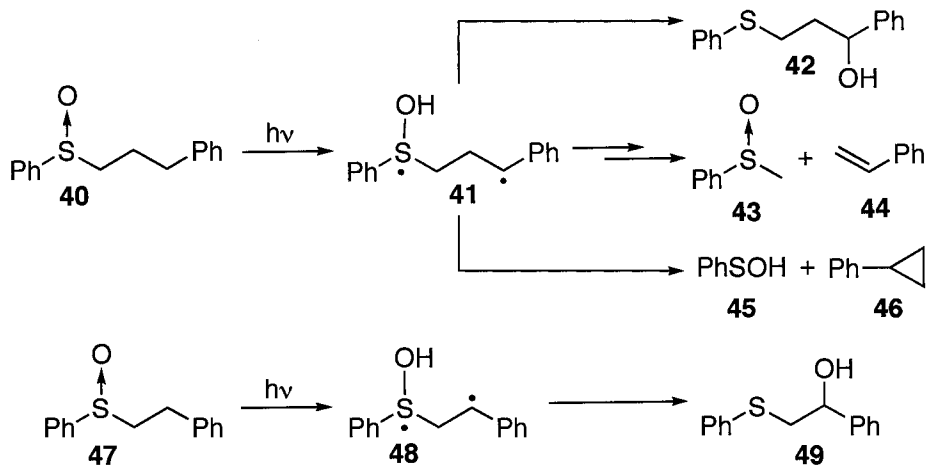


Figure 15. Photolysis to probe hydrogen abstraction mechanism

1.6 Photochemical Deoxygenation of Aromatic Sulfoxides

There are several sulfoxide systems that have been reported to deoxygenate under photochemical conditions. Shelton and Posner observed the earliest reported deoxygenation cases. Shelton showed that *tert*-butyl phenyl sulfoxide produced a small amount of sulfide upon photolysis in 1973.[7] In the same year Posner showed that methyl phenyl sulfoxide and diphenyl sulfoxide also deoxygenated upon photo-irradiation.[22] Following Shelton and Posner's work Still reported photochemical cleavage on a series of thiochromanones. The main photochemical reaction for these compounds was α-cleavage; for only a few compounds the sulfur-oxygen bond cleavage was observed.[23-26] From those experiments it was concluded that deoxygenation is possible only when α-cleavage is energetically disfavored, or when the diradical cleavage product has no choice other than recombining to give the starting material.[12] For this very reason, in most sulfoxides deoxygenation is a minor photochemical process. **DBTO** (compound **5**) is an exception to this rule. Due to its unique structure, α-cleavage is probably a lower quantum yield process, as in phenyl

sulfoxide, and reombination to **DBTO** is probably fast; hence, deoxygenation is the only photoreaction observed (Figure 16).[27-29]

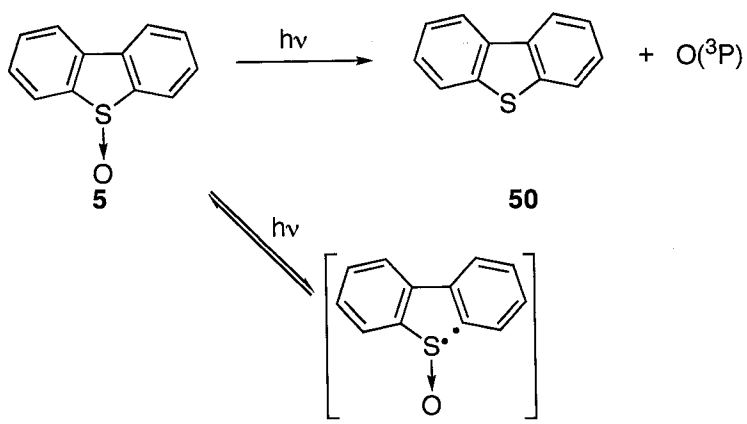


Figure 16. Photochemical deoxygenation of **DBTO**

Several mechanisms were proposed for the deoxygenation of sulfoxides; they include disproportionation, a dimer mechanism, a sulfinyl mechanism, hydrogen abstraction and unimolecular homolytic cleavage. In the next sections each mechanism will be discussed and analyzed. Investigations in the Jenks laboratory suggested the unimolecular S-O bond cleavage described above.[27]

1.6.1 Disproportionation mechanism

Simple disproportionation is common with small sulfoxide compounds, where two molecules of sulfoxide react to produce one molecule of sulfone and one molecule of sulfide. DMSO is one such compound where the disproportionation reaction is observed (Figure 17). In the case of **DBTO** this mechanism could be ruled out since no sulfone was ever detected in the photolysis.

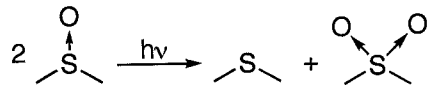


Figure 17. Disproportionation reaction of DMSO

1.6.2 Dimer mechanism

The first proposed photochemical deoxygenation mechanism of sulfoxides was a dimer mechanism proposed by Posner[22] and Shelton[7] independently at nearly the same time. This mechanism proposes formation of a peroxide type sulfoxide dimer from the reaction of a ground state sulfoxide with a photochemically generated triplet sulfoxide. The diradical eventually decomposes to form molecular oxygen and the corresponding sulfide (Figure 18).

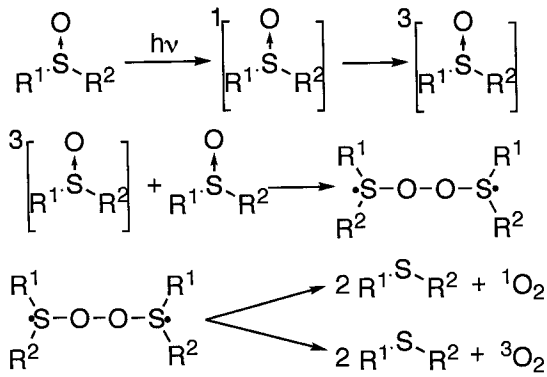


Figure 18. Dimer mechanism for the photo-deoxygenation of sulfoxides

Posner and Gurria suggested a similar mechanism for the deoxygenation of **DBTO 5** in which it forms an excited triplet **DBTO** via intersystem crossing of the initially formed singlet molecule. This triplet molecule then finds another ground state **DBTO** to form the

dimer intermediate **51**. This dimer then decomposes to form **DBT 50** and singlet oxygen (Figure 19).

Involvement of the singlet oxygen was proposed based on the isolation of cyclohexenol when **5** was photolyzed in the presence of cyclohexene as a quencher. According to the authors cyclohexene formed a peroxide intermediate with the singlet oxygen, which eventually decomposed by treatment with sodium iodide.

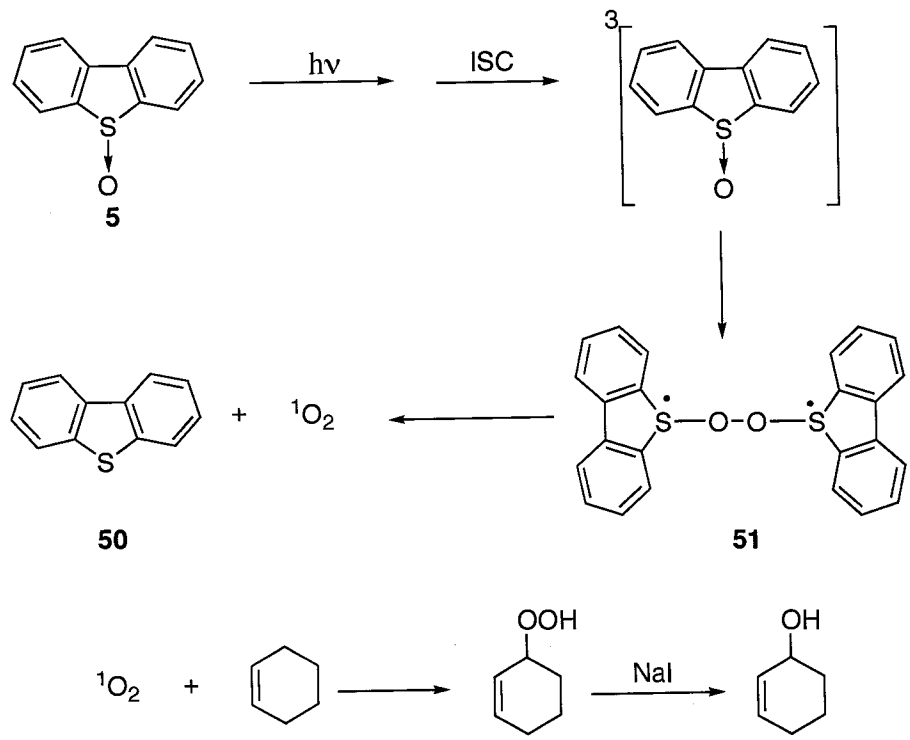


Figure 19. Deoxygenation of **DBTO** by dimer mechanism and trapping of singlet oxygen

The involvement of the triplet state was based on the observation that sensitized experiments only lead to the corresponding sulfide. This argument was further supported by

the fact that piperylene, which is a good triplet quencher, could stop the deoxygenation of diphenyl sulfoxide.

Shelton also suggested the involvement of the triplet sulfoxide for the deoxygenation mechanism of sulfoxide.[7] In evidence for this mechanism, he showed that the quantum yield of diallyl sulfide increased when benzophenone was used as a triplet sensitizer. It is now clear that benzophenone does not have sufficient energy to populate the triplet state of diallyl sulfoxide. Shelton also proposed the formation of a sulfoxide dimer, which was essentially the same mechanistic model proposed by Posner (Figure 19). However, Shelton proposed that the dimer would decompose to form ground state molecular oxygen instead of singlet oxygen as suggested by Posner.

The dimer mechanism was experimentally tested several times since it was proposed. There was much evidence produced against it. The formation of the triplet state of sulfoxide is an essential step in this mechanism. The lifetime of the triplet should be long enough to allow triplet quenching, since the triplet-excited state is forming an excimer with another ground state sulfoxide. However, when **DBTO** was photolyzed in the presence of a triplet quencher such as isoprene, cyclopentadiene, and molecular oxygen, no decrease in the quantum yield of deoxygenation was observed.[28]

1.6.3 Sulfinyl mechanism

The sulfinyl mechanism was suggested by Lüdersdorf *et al.* in the early 1980s on the basis of CIDNP studies of the photochemistry of aryl methyl sulfoxide.[30,31] The key step in this proposed mechanism is α-cleavage to form a free sulfinyl radical and another radical to facilitate oxygen atom transfer (Figure 20).

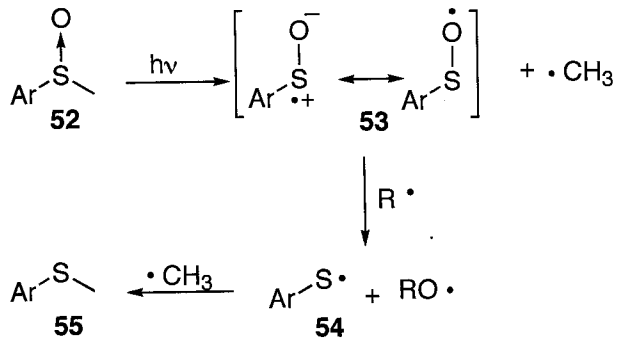


Figure 20. Deoxygenation of a sulfoxide by sulfinyl mechanism.

The sulfinyl mechanism can be ruled out mainly based on the energetics of the sulfinyl radical. The bond dissociation energy of the S-O bond was found to be higher than that of the S-Ph bond. Benson calculated the heat of formation of the phenylsulfinyl radical to be around 13 kcal/mol.[18] The heats of formation for other relevant compounds are all known experimentally.[32] From these values it can be shown that the S-O bond energy is ~102 kcal/mol, whereas the C-S bond is 35 kcal/mol weaker. Also, transfer of the oxygen atom from phenylsulfinyl to a methyl radical (Figure 20, **53** to **54**, R = CH_3) is endothermic by 11 kcal/mol.

1.6.4 Hydrogen abstraction

Another possible mechanism for the deoxygenation of sulfoxides is a hydrogen abstraction mechanism (Figure 21). In this mechanism, the excited sulfoxide abstracts a hydrogen atom from the solvent to form radical **69**, which subsequently decomposes to give

the sulfide either by loss of a hydroxyl radical or by an S_H2 type mechanism where R• radical attacks the hydroxyl group.

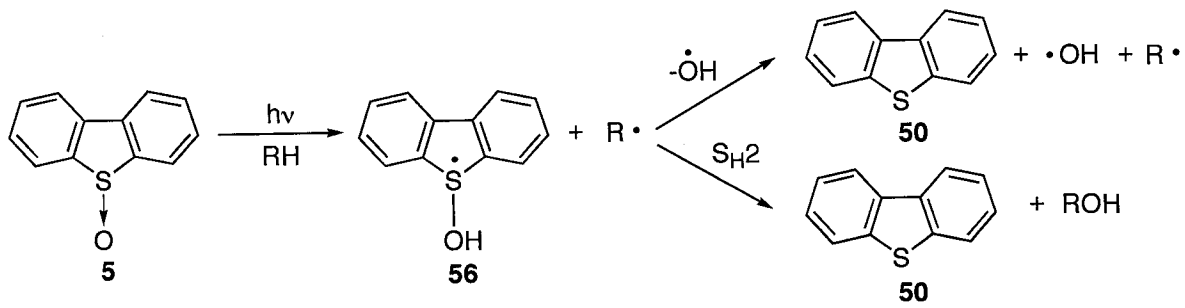


Figure 21. Hydrogen abstraction mechanism

If the hydrogen abstraction mechanism were valid, then the deoxygenation quantum yields of sulfoxides would be highly solvent dependent. One would expect the quantum yield to be higher in solvents that can donate hydrogen atoms easily. This was checked in the Jenks' laboratory but no such solvent dependence was found.[27,28] In Freon 113, which has no hydrogen to abstract, the quantum yield of deoxygenation for **DBTO 5** was found to be 0.0024, which was similar to the quantum yield found in hydrogen atom donating solvents. Although the hydrogen abstraction mechanism was ruled out for unassisted deoxygenation of sulfoxides, a somewhat similar photoassisted bimolecular deoxygenation mechanism was later established by the Jenks group.[33]

Recently Greer *et al.* provided more evidence in favor of the unimolecular deoxygenation mechanism.[29] Sulfoxide **57** and **DBTO** were photolyzed in the presence of different oxygen trapping agents. The oxygen trapped products formed in those photolyses

were compared with the product ratios reported for the reaction for $O(^3P)$ generated from other sources such as the microwave discharge method.[34,35] In Figure 22 the selective oxidation of 2-methylbutane is shown where it forms 2-methyl-2-butanol as the major product. The same substrate produces primary, secondary, and tertiary alcohol in reaction with $O(^1D)$.[36]

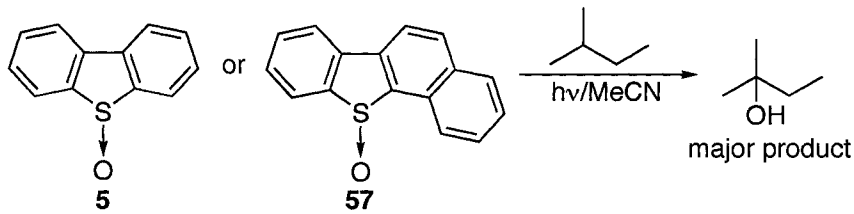


Figure 22. Selective oxidation of 2-methylbutane in the photolysis of sulfoxides **5** and **57**

1.7 Bimolecular Photoreduction of Aromatic Sulfoxides

A photoassisted bimolecular mechanism for the deoxygenation of aromatic sulfoxides was first proposed by Kropp in the early 1990s to explain the result of a photochemical reduction.[37] Their investigated photolysis and postulated mechanism is shown in Figure 23. The photolysis of 2-norbornyl phenyl sulfoxide **58** in methanol produced only a trace amount of 2-norbornyl sulfide **59** . The yield of the sulfide **59** increased to 64% upon the addition of 0.2 M sodium methoxide. The proposed mechanism involves the donation of an electron from sodium methoxide to the excited state of sulfoxide **58**. Proton transfer from the solvent produces intermediate **60**, which subsequently loses the hydroxyl radical to produce the sulfide.

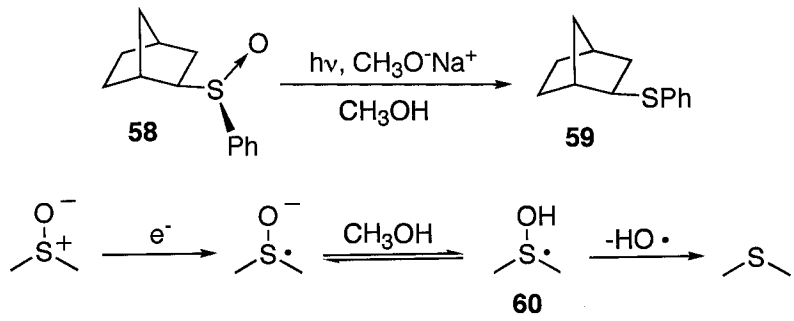


Figure 23. Photoassisted deoxygenation of 2-norbornyl phenyl sulfoxide

Recently Cubbage and coworkers studied the bimolecular photoreduction of sulfoxides in detail to elucidate its mechanism.[33] The proposed mechanism was based on Kropp's model presented above. Excited diphenyl sulfoxide **23** was proposed to produce radical anion **61** after an electron transfer from the methoxide anion. Then this radical anion could capture a proton from the solvent to produce hydroxysulfuranyl radical **62**. Radical **62** can either form sulfide **63** by a direct homolytic cleavage or it can lose the hydroxyl group by heterolytic cleavage to form **64**. The first process was calculated to be endothermic by 11 kcal/mol,[38,39] whereas the second process in aqueous solution is somewhat less endothermic, about 5 kcal/mol.[40] Compound **64** can abstract a hydrogen either from methanol or from some other radical to form the radical cation **65**. The S-H bond strength of **65** was calculated to be about 78 kcal/mol, about 17 kcal/mol less than the O-H bond strength of methanol. In the next step, methoxide can easily abstract the proton from **65** to form sulfide **63** via an exothermic reaction. Although the heterolytic cleavage mechanism was favored, the homolytic cleavage mechanism could not be completely overruled. The reaction was also carried out in electron donating sensitizers like aniline or carbazoles, and the solution was photolyzed at a wavelength where the sulfoxide does not absorb. These reactions also

produced the sulfide, and the authors suggested a similar mechanistic pathway after the electron transfer step for these sensitized reactions.

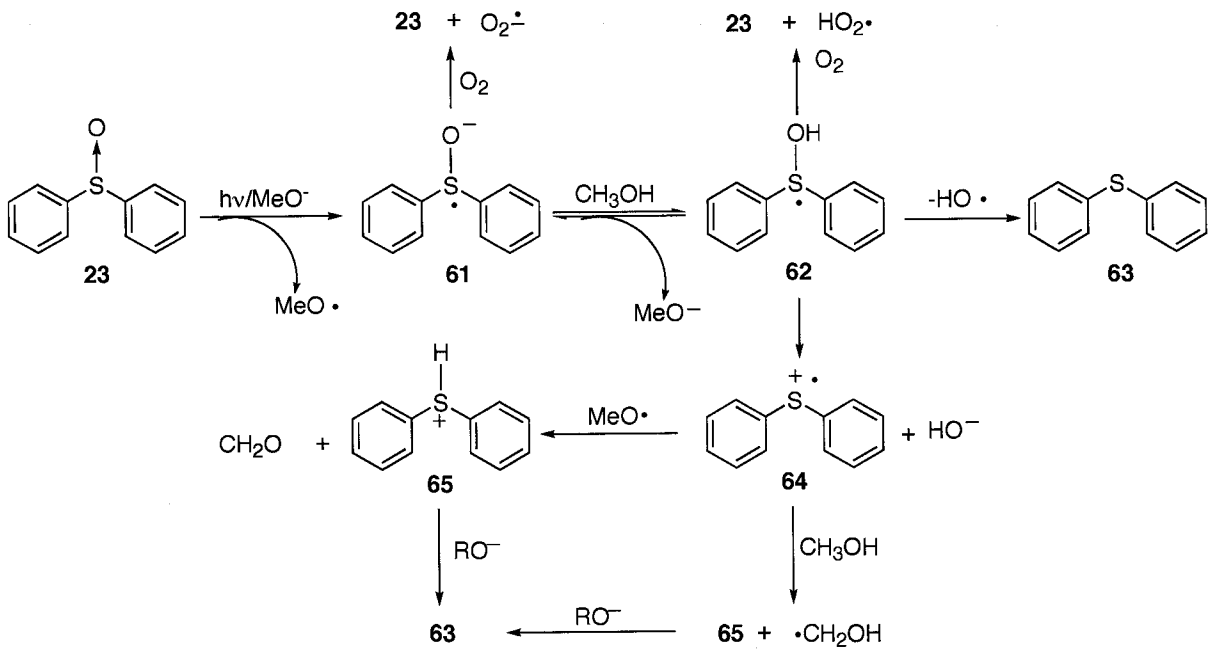


Figure 24. Proposed mechanism for bimolecular photodeoxygenation of sulfoxides

1.8 Stereomutation of Sulfoxides

As mentioned earlier, the sulfoxide group is chiral when two different groups are attached to the sulfur atom. Due to this unique property, sulfoxides are very useful in organic chemistry as chiral auxiliaries. Chiral sulfoxides can be racemized photochemically (Figure 25).

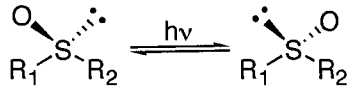


Figure 25. Stereomutation of sulfoxides

There are two different mechanisms proposed for photochemical stereomutation of sulfoxides. The first one is the α-cleavage reaction followed by recombination of the radical pair (Figure 26).

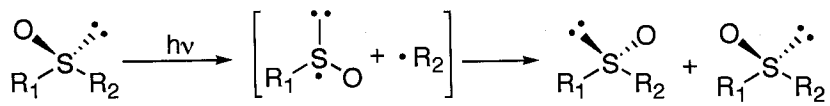


Figure 26. Stereomutation of sulfoxides by α-cleavage reaction

The second proposed mechanism is via a direct inversion (Figure 27). In the excited state of the sulfoxide inversion is possible when the inversion barrier is quite small. There is evidence for both of the mechanisms in the literature but α-cleavage has been studied more extensively than the inversion mechanism. However, more compelling evidence for the inversion mechanism has been established in recent years.[10,15,41,42]

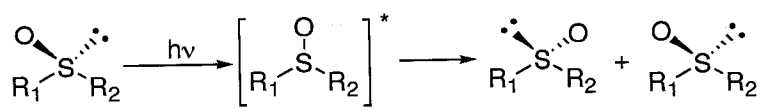


Figure 27. Direct inversion mechanism for the stereomutation of sulfoxides

Mislow and Hammond were among various scientists who have reported both direct and sensitized photostereomutation of sulfoxides.[43-47] From those reports, it was concluded that there was substantial structural effect on the stereomutation. Aryl groups were proved to be a requirement for the stereomutation, as dialkyl sulfoxides decomposed without forming any racemized product. Cooke and Hammond studied the photoreaction of *p*-tolyl methyl sulfoxide. With naphthalene as a sensitizer, they observed a higher quantum yield for racemization compared to the results obtained from direct irradiation. Since naphthalene has a lower singlet energy than the sulfoxide, the authors suggested involvement of an exciplex in the stereomutation step.[47,48] Based on the sensitization experiments the authors suggested involvement of the singlet excited state of naphthalene in the exciplex formation (Figure 28).

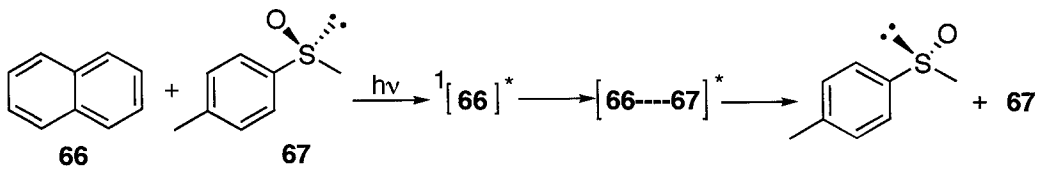


Figure 28. Stereomutation of *p*-tolyl methyl sulfoxide via exciplex formation

Guo and Jenks investigated the steromutation of sulfoxides in further detail.[15] In their report they studied racemization of different aryl alkyl sulfoxides **47**, **68** and **67** (Figure 29). Except for aryl benzyl sulfoxide **68,** the difference between the quantum yields of decomposition and racemization was very high. For sulfoxides **47** and **67**, the quantum yield of rotation was more than 40 times higher than the quantum yield of decomposition. This suggests an alternative pathway other than α-cleavage for the stereomutation of sulfoxides. For sulfoxide **68**, the α-cleavage and the subsequent decomposition was driven by the

stability of the benzyl radical, which could not be formed in sulfoxides **67** and **47**. From these results the authors suggested that the major pathway for stereomutation of some sulfoxides was direct inversion, although the α-cleavage mechanism could not be ruled out completely.

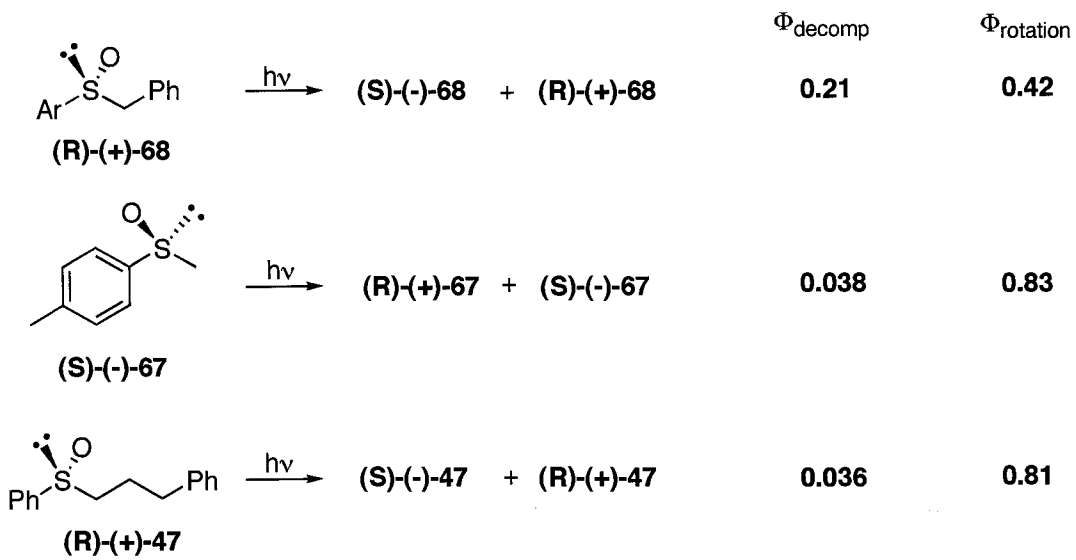


Figure 29. Stereomutation of some aromatic sulfoxides in *t*-butanol

Recently, Vos and Jenks provided more compelling evidence for the pyramidal inversion mechanism in aromatic sulfoxides.[41] An aryl alkyl chiral sulfoxide **(R_S, S_C)-69** (nomenclature was based on optical rotation of sulfur and carbon atoms, which were subscripted) was designed in such a way that an α-cleavage would produce four different stereoisomers including the starting material (Figure 30). By using clever detection techniques, the authors could identify each of the stereoisomers. The results showed a significantly higher conversion to stereoisomer **(S_S, S_C)-69**, which can be formed via direct

inversion or α-cleavage over the formation of isomers **(S_S, R_C)-69** and **(R_S, R_C)-69**, which can be formed only via α-cleavage.

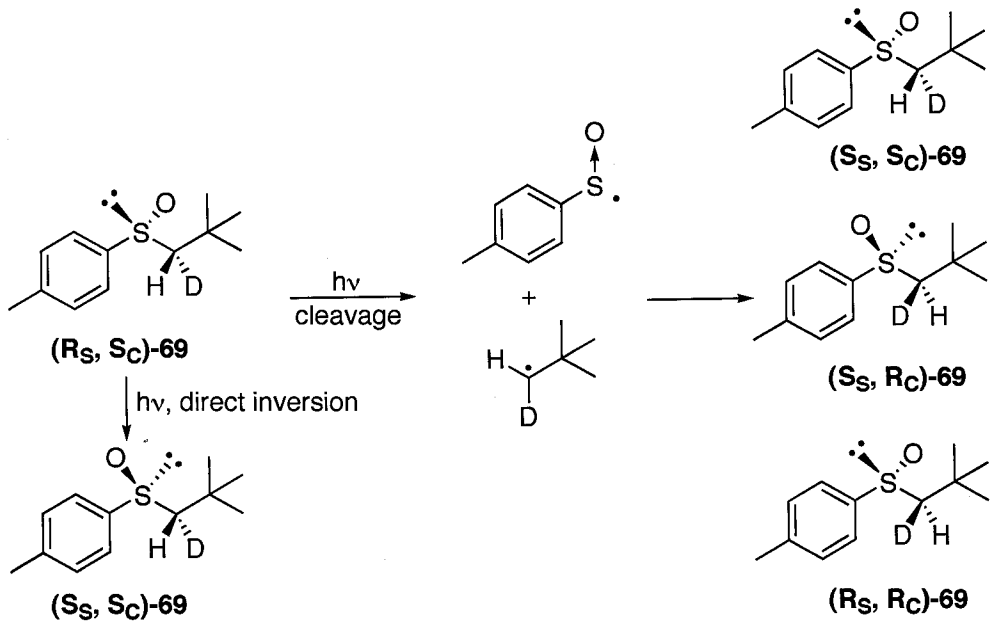


Figure 30. Stereomutation of chiral sulfoxide via nonradical pathway

1.9 Photophysics of Aromatic Sulfoxides

The photophysics of sulfoxides has not been studied as extensively as the photochemistry. However it is important to know the singlet and triplet energies of sulfoxides to completely understand their photochemistry. Jenks and coworkers reported photophysical properties of several alkyl aryl and diaryl sulfoxides.[42,49] Fluorescence and phosphorescence were obtained at 77 K in EPA (ether, isopentane and ethyl alcohol in 5:5:2 mixture) or MCH (methyl cyclohexane) glass. However, it must be noted that only a few of the sulfoxides showed fluorescence at 77 K. In their 1994 paper, Jenks and coworkers reported the triplet energies of selected aromatic sulfoxides.[49] Some of those systems and

their triplet energies (E_T) are shown in Figure 31. From these results it is clear that the triplet energies of aromatic sulfoxides are a few kilocalories per mole higher than their ketone analogues, and a few kilocalories per mole lower than the corresponding aromatic systems without the sulfoxide functional groups. It must be noted that the phosphorescence of aromatic sulfoxides is very weak and most of the phosphorescence quantum yields are <0.01. On the other hand, their sulfide analogues have a very high quantum yield of phosphorescence (usually >0.1), and their triplet energies are generally lower than sulfoxides. The triplet states of the aromatic sulfoxides were described as aromatic $\pi\pi^*$ states that are strongly perturbed by the sulfoxide moiety based on several factors including the strong heavy atom effect observed for sulfoxide **73**.

These results are essential in order to understand some of the very important facets of sulfoxide photochemistry. Many sensitizers, which influenced sulfoxide photochemistry, have lower triplet energies than sulfoxides. These reactions were previously attributed to the energy transfer sensitization but they are likely to follow some other mechanisms such as electron transfer.[7,30,50,51]

Sulfoxide **5**, which will be discussed in detail in the next two chapters, has a triplet-energy of about 61 kcal/mol. All evidence for the photochemical deoxygenation of this sulfoxide indicates the formation of a triplet oxygen atom O(^{3}P) but the S-O homolytic bond breaking energy was calculated to be about 75-77 kcal/mol.[52] From this, it is clear that the bond breaking process was not coming from the lowest excited triplet state. This problem and the possible answer will be discussed in the next chapter.

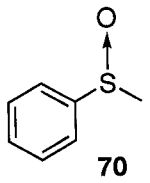
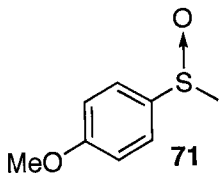
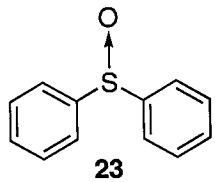
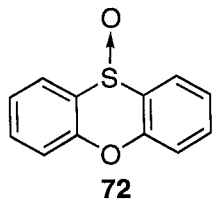
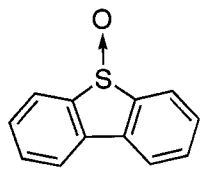
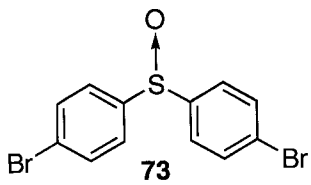
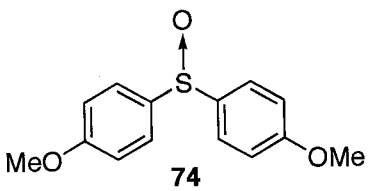
	Singlet Energy (kcal/mol)	Triplet Energy (kcal/mol)	$\Phi_{phosphorescence}$
 **70**		81	<0.001
 **71**	99	80	0.018
 **23**		78	≤0.004
 **72**	91	79	0.014
 **5**	85	61	0.040
 **73**		76	0.061
 **74**		77	0.10

Figure 31. Photophysical properties of some aromatic sulfoxides from emission spectra[49]

In another effort, Lee and Jenks tried to rationalize the low quantum yield of fluorescence and phosphorescence in aromatic sulfoxides.[42] In their report they studied several different aryl methyl sulfoxides. The methyl group was intentionally chosen to suppress α-cleavage reaction.[15,17] The aryl groups were highly conjugated systems like naphthalene, biphenyl, and pyrene. Fluorescence yields were measured both at room temperature and at 77 K in frozen glass. The fluorescence quantum yields were very low in both environments compared to their parent aromatic systems. At the same time significant pyramidal inversion was observed for these sulfoxide systems. Since no inversion was observed in sensitized conditions, it was concluded that the inversion occurs from the singlet excited state of the sulfoxides. Combining these two observations, the authors concluded that the reason for a low fluorescence quantum yield was probably due to the high quantum yield of racemization.

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CHAPTER II

PHOTOCHEMISTRY AND PHOTOPHYSICS OF HALOGEN-SUBSTITUTED DIBENZOTHIOPHENE OXIDES

Based on a paper published in the *Journal of Organic Chemistry*[1]

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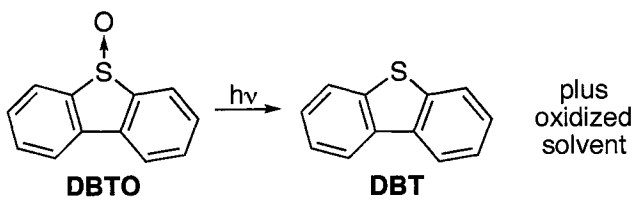
Abstract: Dibenzothiophene-5-oxide (**DBTO**) cleanly produces dibenzothiophene (**DBT**) on direct photolysis, but with very low quantum yield. A proposed mechanism involves scission of the S-O bond which is coupled to an intersystem crossing step, thus producing the sulfide and $O(^3P)$ via a unimolecular pathway. To test this hypothesis, heavy atom substituted DBTOs were prepared and photolyzed. Iodo-, bromo-, and chloro- substituted DBTOs show higher quantum yields for deoxygenation than does the parent molecule, in the order consistent with an intersystem crossing-related heavy atom effect. 2–Iododibenzothiophene also undergoes photochemical deiodination. Phosphorescence data are consistent with heavy-atom assisted intersystem crossing.

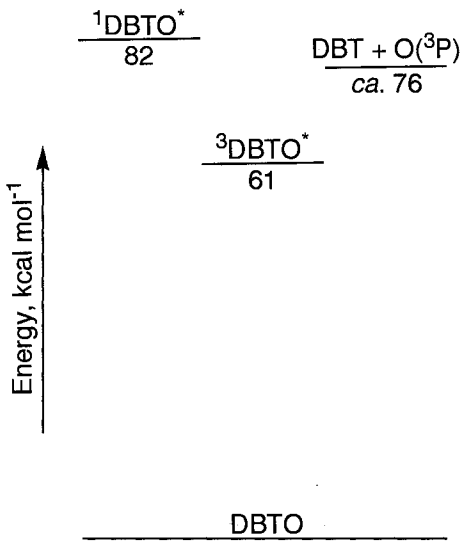
2.1 Introduction

One of the fundamental photochemical reactions of aromatic sulfoxides is deoxygenation to form the corresponding sulfide on direct irradiation.[2-12] Though the sulfide is usually a minor component of the product mixture, in the photolyses of dibenzothiophene-5-oxide (**DBTO**) and some of its derivatives, it is the major sulfur-containing product.[3,13-16] From a mechanistic perspective, many experimental results are consistent with simple S-O cleavage that yields the sulfide and $O(^3P)$.[13,14,16] For example, product studies based on the oxidation of solvents and other reactive traps in the presence of **DBTO** are consistent with expectations for $O(^3P)$. Though no direct evidence has been obtained for the formation of this reactive intermediate, the evidence pointing towards a unimolecular mechanism is compelling.[9,13,16]



Thus, **DBTO** derivatives are promising candidates as photochemical precursors for the study of $O(^3P)$ chemistry in solution.[14] Other methods of oxygen atom formation invariably either require very high energy irradiation or precursors that are themselves oxidants (e.g., ozone). In order to further test and exploit the $O(^3P)$ hypothesis, however, improved substrates are needed because the chemical quantum yield for **DBTO** photolysis is less than 0.01.[16]

One rationalization of the low quantum yield is that the deoxygenation proceeds by a mechanism in which S-O bond stretching must be accompanied by intersystem crossing at some point before complete bond scission. Such a mechanism is consistent with the energetics of the reaction for **DBTO**, as illustrated in Scheme 1. The fluorescent singlet energy of **DBTO** is about 82 kcal mol^{-1}, and the phosphorescent triplet energy is about 61 kcal mol^{-1}.[17] The S-O bond dissociation energy, forming $O(^3P)$, has been estimated to be 75-77 kcal mol^{-1} using computational methods.[18,19] These energetics imply that **DBTO** must be on a path towards scission when isc occurs and not ever reach the phosphorescent triplet, which lacks sufficient energy for S-O dissociation. At the far end of the mechanistic continuum suggested by this idea is the notion that initial scission could result in an ion pair of $\mathbf{DBT}^{\bullet+}$ and O^-, followed by back electron transfer to the ground state of **DBT** and $O(^3P)$.



Scheme 1. Relative energetics for **DBTO** excited states[17] and S-O dissociation.[18]

To the extent that one accepts the unimolecular scission hypothesis and that $O(^3P)$ is the reactive intermediate, two goals present themselves for optimization of **DBTO**-like

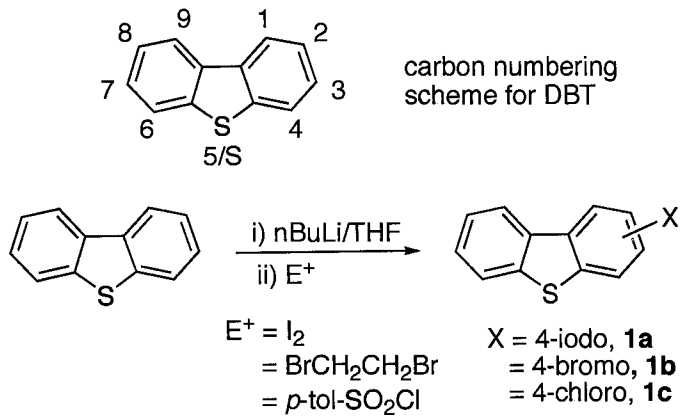
sources of oxygen atoms: (1) a red-shifting of the absorption such that the extinction coefficient is large at more convenient laser lines, such as 355 nm; and (2) an increase in the efficiency of the reaction, so as to generate a higher concentration of $O(^3P)$ with a given pulse of light. In this paper we address a series of experiments aimed mainly at the second of these goals.

One reasonable strategy towards increasing the probability of all isc events is heavy atom substitution. Heavy atom substitution facilitates spin orbit coupling, and hence increases the probability (and the absolute rate constants) for both radiative and non-radiative spin-inverting processes.[20,21] In this paper, we report how adding halogen and acetyl substituents affects the photochemistry and emission of the **DBTO** nucleus.

2.2 Results

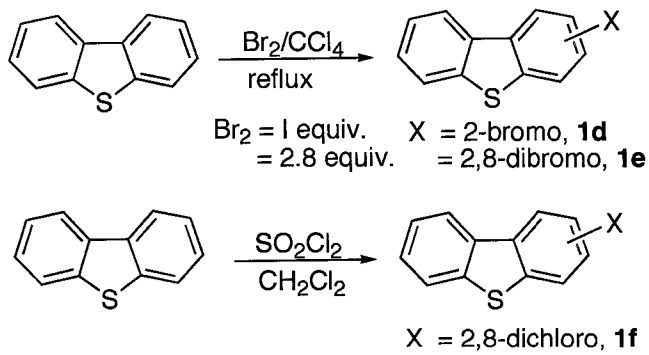
Compound Preparations

Substituted DBTs (**1a-c**) were prepared from **DBT** by lithiation and quenching with an electrophile by method of Katritzky.[22] Iodine, 1,2-dibromoethane, and *p*-tolylsulfonylchloride were the electrophiles used to make compounds **1a-c** respectively (Scheme 2). Bromine was used as an elctrophile initially to prepare compound **1b** but the purifying the reaction mixture was proved difficult. As an alternative 1,2-dibromo ethane was used as a reagent and it gave a clean reaction.[23]



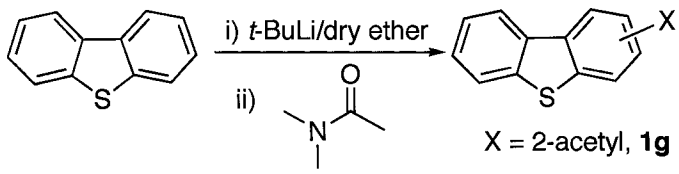
Scheme 2 Compound numbering and preparation of 4-halo DBTs

2-Bromo and 2,8-dibromo DBTs **1d-e** were prepared by the method of Shimomura.[24] DBT and bromine were refluxed in carbon tetrachloride. For **1d**, one equivalent of bromine was used, and for **1e**, 2.8 equivalent of bromine was used. 2,8-Dichloro DBT **1f** was prepared by method of Savin.[25] Although the original method described preparation of the corresponding sulfoxide, no sulfoxide could be isolated in the reaction mixture. However, this procedure gave decent yield of compound **1f**.



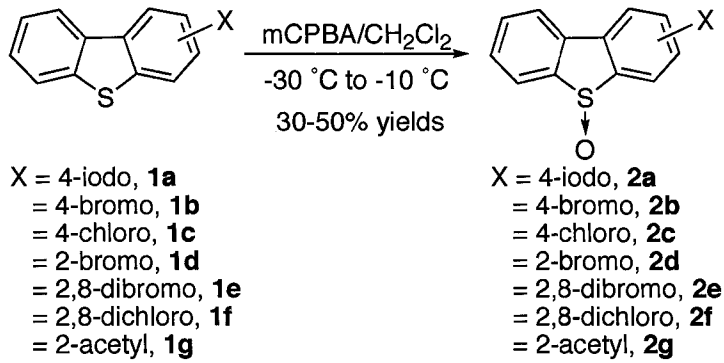
Scheme 3. Preparation of sulfides **1d-f**

2-Acetyl DBT **1g** was prepared by method of Campaigne.[26] Compound **1d** was lithiated using *t*-butyllithium in dry ether and the lithiated DBT was quenched with *N,N*-dimethylacetamide (Scheme 4).



Scheme 4. Preparation of 2-acetyl DBT

Compounds **1a-g** were oxidized using mCPBA at moderately low temperature, to give the corresponding DBTOs (**2a-g**) in satisfactory unoptimized yields.[27]



Scheme 2. Preparation of substituted DBTOs.

Luminescence

Fluorescence spectra of the **DBT** derivatives **1a-f** at room temperature in cyclohexane were very similar to that of **DBT** (Figure 1), save for the intensity. Quantum yields are

reported in Table 1. The acetyl derivative **1g** did not detectably fluoresce; neither did any of the **DBTO** derivatives **2a-g**.

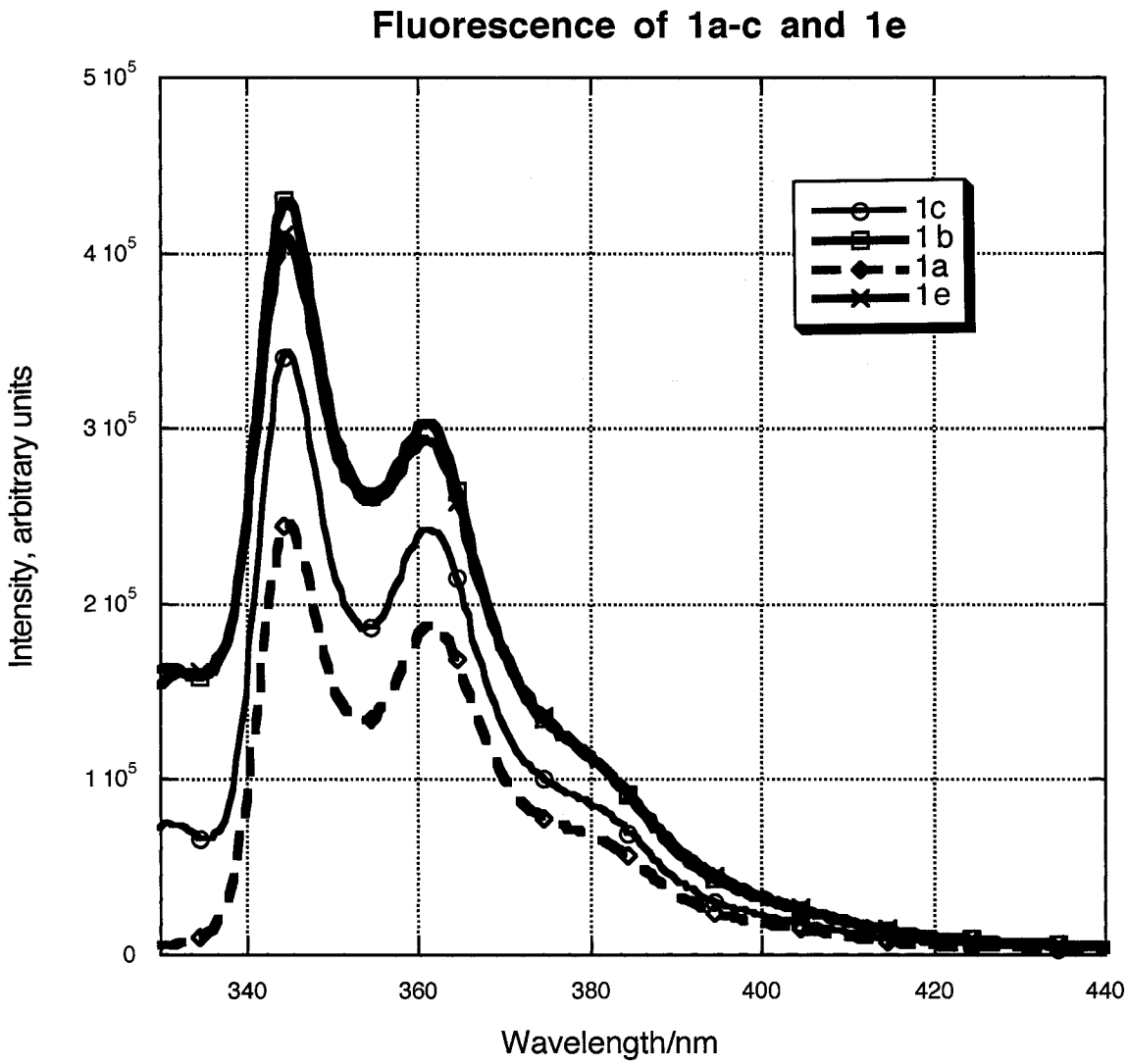


Figure 1. Fluorescence spectra of halogenated DBTO

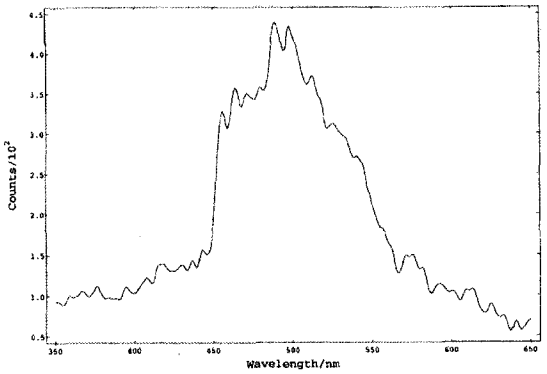
Table 1. Luminescence quantum yields.

Compound	Φ_f[a]	Φ_p[b]
DBT	0.09[c]	
1a	0.018	
1b	0.045	
1c	0.036	
1e	0.057	
DBTO		0.001
2a		0.065
2b		0.049
2g[d]		0.55

[a]Naphthalene in cyclohexane was used as the actinometer, with excitation at 265 nm.[28] Spectra were obtained in cyclohexane at room temperature. Data were not obtained for **1f**. Otherwise, unlisted compounds did not detectably fluoresce. [b]Benzophenone used as an actinometer with excitation at 265 nm.[28] Spectra were obtained at 77 K in EPA frozen organic glass. [c] Literature value.[29] Measured with 280 nm excitation to avoid a minimum in the absorption spectrum.

At 77 K in EPA glass,[30] **DBTO** has a weak phosphorescence.[17] Similar, but somewhat more intense, spectra were obtained from **2a** and **2b**, and approximate quantum yields were measured with respect to benzophenone.[28] The spectroscopic triplet energies do not vary widely within the series. These weak spectra are characterized by an onset near 450 nm, and are easily obscured by the much more phosphorescent corresponding sulfides, whose spectra have an onset near 400 nm.[31] The acetyl derivative **2g** is highly phosphorescent at 77

K. However, its unstructured spectrum is considerably different, with an onset near 370 nm (Figure 2).[32]



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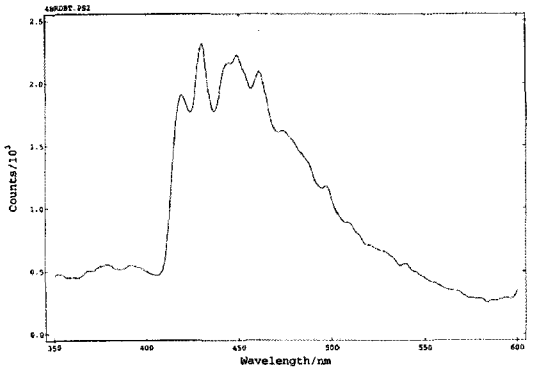

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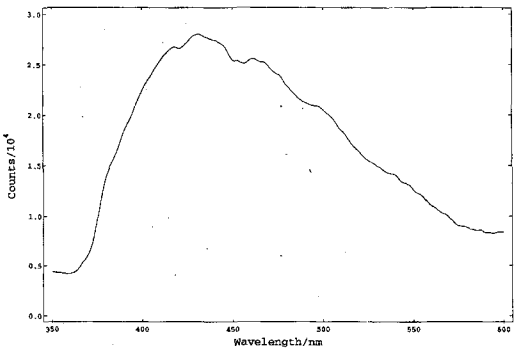


c)

Figure 2. Phosphorescence spectra of a) **2a**, b) **2b** and c) **2g** in EPA glass at 77K

Photolyses

Photoreactions of sulfoxides **2a-g** were carried out in acetonitrile using initial concentrations ranging from 1.5 – 4 mM. The absorption spectra have maxima near 320 nm, so all compounds were excited at that wavelength (±12 nm) using a Xe-arc lamp filtered through a monochromator. Product analysis was done when the reaction had reached no greater than 10% conversion.

The acetyl derivative **2g** was apparently inert to photolysis, but the other compounds **2a-2f** provided the corresponding deoxygenated sulfides. The quantum yields of sulfide formation in acetonitrile were measured, relative to the Type II reaction of valerophenone, and are reported in Table 2.[33] The precision of the results, as reflected in the standard deviations from multiple runs, demonstrates that these differences, though modest, are statistically significant.

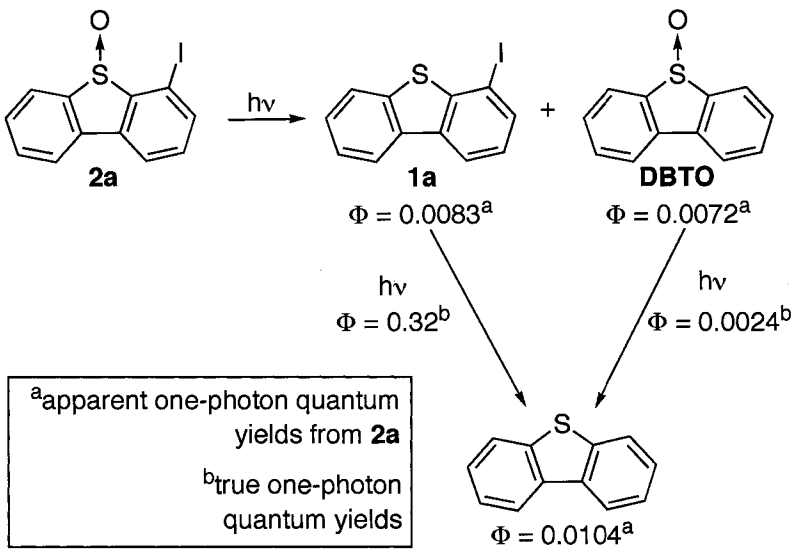
Table 2. Quantum yields of deoxygenation.

Compound	Φ_{deox} [a]
2a	0.0083[b] ± 0.0001[c]
2b	0.0053 ± 0.0001
2c	0.0045 ± 0.0006
2d	0.0056 ± 0.0004
2e	0.0093 ± 0.0009
2f	0.0034 ± 0.0003
2g	~0
DBTO	0.0024[d]
2b in benzene	0.0220
2b in cyclohexene	0.10
2b in 1:9 cyclohexene/acetonitrile	0.010

[a] Data were measured by appearance of the sulfide. Solvent is CH_3CN, unless otherwise noted. The actinometer was acetophenone formation from valerophenone.[33] [b] This is the apparent one-photon yield for formation of **1a**, but is a lower limit, due to the efficient photodeiodination of this product. [c] Quoted error bars are standard deviations. Literature value.[16]

In addition to the expected sulfide **1a**, the iodosulfoxide **2a** produced dehalogenated products, i.e., **DBTO** and **DBT**. Such dehalogenations were not observed from any other sulfoxide. Over the course of extensive irradiation of **2a**, the ratio of the products varied with conversion, with **DBT** building up at the expense of the other two, consistent with its formation being via secondary photolysis.

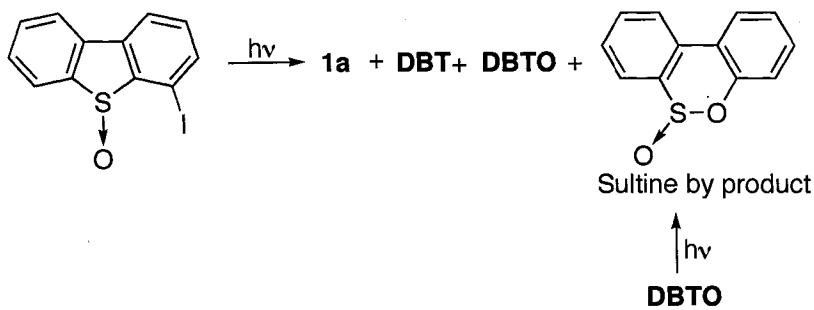
Quantum yield measurement is thus more complicated for **2a**, because of the two primary photochemical reactions: deoxygenation and dehalogenation. Additionally, both secondary reactions lead to **DBT**. However, the quantum yields of the secondary reactions could be measured directly and the data are presented in Scheme 3.



Scheme 3. Photochemistry and quantum yields for photolysis of 2a in acetonitrile.

Because the quantum yield of deiodination of **1a** is so much larger than that of any of the other processes, the appearance of **DBT** is approximately linear with time during the early stages of the photolysis, and thus apparent one-photon quantum yields are obtained for the two true primary products (**1a** and **DBTO**) and the secondary product **DBT**. The apparent quantum yields for the primary products are lower than the actual values, which could not be obtained. Because of the efficient conversion of **1a** to **DBT**, it can be concluded that the actual primary quantum yield for dehalogenation of **2a** is substantially greater than that for deoxygenation.

To ensure the validity of the interpretations here, photolyses were carried out to higher conversions. To demonstrate the two-photon pathway to **DBT**, the irradiations were done using different irradiation wavelengths, using RMR-3000 or RMR-3500 fluorescent tubes, centered at about 300 or 350 nm, respectively, in a Rayonet mini-reactor. The data are shown in Figure 3 with the abscissa normalized to conversion of **2a**, rather than time, for easier comparison of the two. Because of the extended photolysis times required (25 and 37 hours, respectively), the photolyses were stopped when none of the starting material remained. Nonetheless, high yields (84% and 91%) of **DBT** were obtained. Because of the relatively high initial concentration of **2a** (*ca.* 4 mM), some oxidized **DBTO** was also obtained. This product has been previously observed in from **DBTO** itself[34] and has been assigned the structure of the corresponding sultine (sulfinic ester). This compound was not sulfone since its retention time in GC was different from sulfone. The structure of this compound is shown in scheme 4.



Scheme 4. Formation of sultine by product in the photolysis

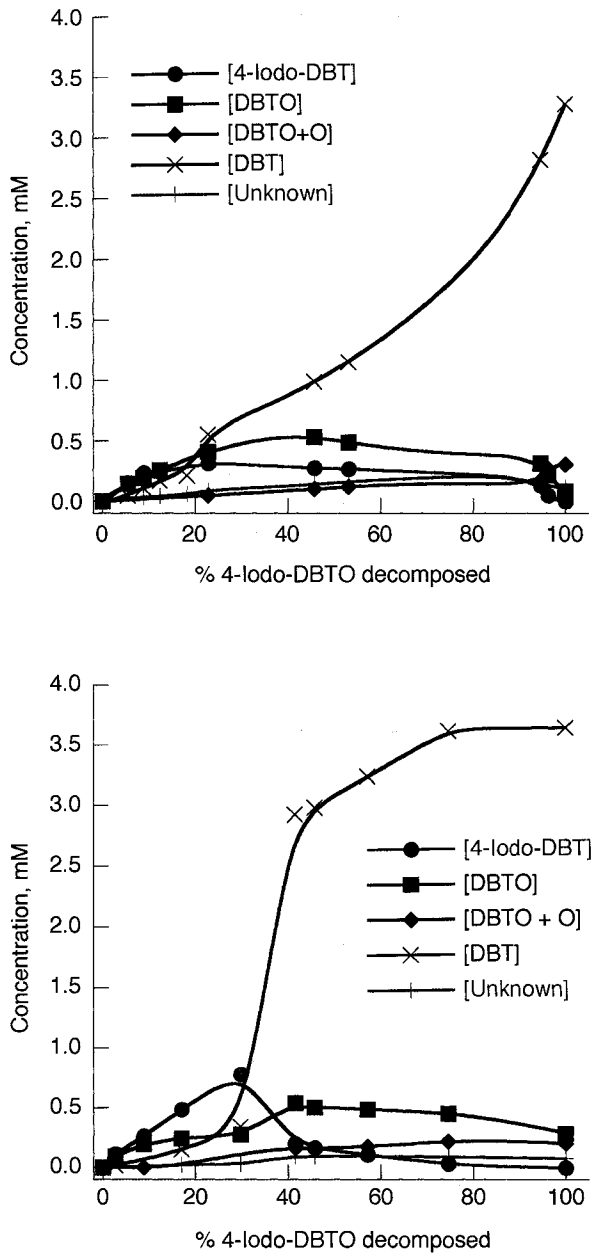


Figure 3. Products observed on photolysis of **2a** in acetonitrile, with initial concentration of 4.0 mM. The abscissas are normalized to percentage decomposition of **2a**. The lines are smooth fits to help draw the eye and of no physical significance. Top: Excitation from 300 nm fluorescent tubes. Total time was 1500 min. Bottom: Excitation from 350 nm fluorescent tubes. Total time was 2200 min.

The fraction of light absorbed by each compound changes with the time, as indicated in the figure 3. The extinction coefficients for absorption in the 300-320 nm range rank in the order **2a** > **DBTO** > **1a** > **DBT**. Near 350 nm, the order is the same, but the sulfoxides have much greater extinction coefficients than the sulfides. Although after significant percentage of decomposition, the other compounds absorb more light since their concentrations also increase. Additionally, some discoloration of the solutions occurs, consistent with the formation of a small quantity of molecular iodine, but no effort was made to document the colored material. The essential result, however, is the clear induction period associated with formation of **DBT**, which indicates that it is a secondary photoproduct. In addition, the comparable initial yields of **DBTO** and **1a** at low conversion are reflective of the comparable quantum yields of their formation reported in Scheme 3.

The photochemistry of **2b** was examined in benzene and cyclohexene, to verify that the same type of intermediate was formed as in photolysis of **DBTO**. Product studies carried out by the methods previously reported,[15,16] showed the same products of solvent oxidation, in nearly identical yield, were obtained using either **DBTO** or **2b**. The major oxidized product from benzene is phenol, while cyclohexene yields both cyclohexenol and cyclohexene oxide in very similar amounts.[15,16] The quantum yields were also measured and are reported in Table 2.

2.3 Discussion

The data presented here support the essential hypotheses used in designing the experiments. The existence of a heavy atom effect is demonstrated by the phosphorescence data, in which the iodosulfoxide and bromosulfoxide have considerably greater quantum

yields than **DBTO**. In line with expectations, Cl-substitution has little heavy atom effect. Compounds **2c** and **2f** are not phosphorescent, and their deoxygenation quantum yields are only marginally higher than that of **DBTO.** Thus **2c** and **2f** are good control compounds to show that the larger effects in other compounds do not come from a more mundane source, such as desymmetrizing of the chromophore.

Greater phosphorescence yields can result either from greater efficiency in formation of the triplet, or from a greater fraction of triplets undergoing emissive decay, or both. We cannot distinguish among these possibilities. Nonetheless, there is some evidence (see below) for a significant triplet yield for **2a**. In any case, it is quite reasonable to assign the greater phosphorescence quantum yield to heavy-atom-assisted mechanisms. It should also be noted that the fluorescence yields of the substituted DBTs are lower than that of **DBT** itself – consistent with a heavy atom effect – though the value for **1c** is lower than might be expected for a simple trend among the halogenated compounds.

In a previous work,[16] we reported that the use of oxygen, isoprene, or cyclopentadiene as potential triplet quenchers did not lower the quantum yield of **DBTO** deoxygenation. This showed that deoxygenation does not proceed through a typically long-lived triplet state of the sulfoxide. The facts that triplet quenchers do not lower the efficiency of deoxygenation and the triplet excitation energy is below the energy required to carry out S-O scission imply that a higher yield of the spectroscopic triplet would not be inherently favorable for deoxygenation yields. Thus, the classic increase of the intersystem crossing rate in arenes by heavy atoms could be counterproductive. Nonetheless, small but reproducible and significant increases in deoxygenation are obtained with the iodosulfoxide **2a** and the bromosulfoxides **2b**, **2d**, and **2e**, relative to **DBTO** and the chlorinated sulfoxides.

Especially taking into account that it is likely that the triplet yields of **2a**, **2b**, **2d**, and **2e**, are higher than that of **DBTO**, we assert that the increased quantum yields for deoxygenation in this series of compounds are consistent with the idea that S-O scission is coupled with intersystem crossing by way of an excited state surface crossing to a dissociative triplet state. Similar mechanistic assertions have been discussed, for example, in the extensive published work on the photodissociation of aryl halides.[35] Recent computational papers by Liu and coworkers derives explicit potential energy curves for halobenzenes and discuss the surface crossings promoted by halogen-induced spin orbit coupling in detail.[36,37]

Another mechanistic extreme that cannot be eliminated is the photodissociation to an ion pair, presumably $\mathbf{DBT}^{\bullet+}/O^{\bullet-}$, followed by back electron transfer that leads to **DBT** and ground state $O(^3P)$. This back electron transfer pathway would naturally compete with simple recombination and thus could also result in a low quantum yield. If the ion pair is born in a singlet state, then heavy atom substitution on the **DBT** moiety might facilitate the back electron transfer pathway and raise the quantum yield of $O(^3P)$ formation.

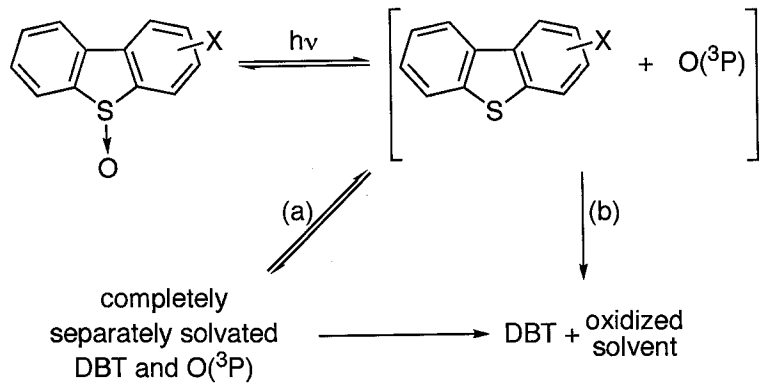
The three bromo-substituted compounds were investigated to determine empirically whether a higher quantum yield could be obtained by moving the substituent or adding a second one. From the practical perspective of trying to use these compounds in independent studies of oxygen atom chemistry, the differences are not especially significant, though adding a second bromine does enhance reactivity.

Iodinated sulfoxide **2a** showed high quantum yield of phosphorescence compared to **DBTO** and it was expected to show similarity in the case of deoxygenation quantum yield. But the initial attractiveness of the higher quantum yield for **2a** is quickly quashed by the

complications involved with the dehalogenation reaction. The fact that only it and its corresponding sulfide **1a** undergo the photodehalogenation reaction suggests that this is an orthodox homolysis reaction, which is usually assigned to triplet state chemistry. (See, for example, refs [38] and [39].) The bond energy for aryl iodides is of the order of 64 kcal mol^{-1},[38,39] That is just a few kcal mol^{-1} higher than the energy of the spectroscopic triplet of **2a**, probably within reach at room temperature, given the moderate quantum yield. The triplet energies of the **DBT** derivatives is about 70 kcal mol^{-1},[17] which is above the energy required for C-I homolysis and presumably contributes to the higher quantum yield for deiodination of **1a**.

On the other hand, arene-Br bond energies are near 70 kcal mol^{-1}.[38,39] With triplet energies of the order of 60 kcal mol^{-1}, it is not surprising that **2b**, **2d**, and **2e** do not debrominate competitively with deoxygenation. On the other hand, exhaustive photolysis might have led to dehalogenation of the corresponding sulfides, given their higher triplet energies.

The solvent dependence on the quantum yield observed for **2b** is consistent with our previous observations for **DBTO**,[16] though with values all somewhat larger than for the parent. We interpret the solvent dependence in terms of a model suggested in Scheme 5.



Scheme 5. A model to explain solvent dependence on quantum yields based on competition between reaction with solvent and **DBT**.

On scission, $O(^3P)$ is formed in the immediate vicinity of **DBT**. As a result, the reactive intermediate may immediately react with the sulfide to reoxidize it, diffuse away from the sulfide before reacting with anything, or react with solvent before escaping from the cage. To the extent that one solvent reacts with $O(^3P)$ faster than another one, the observed quantum yield will be higher. Acetonitrile is not a particularly active substrate for reactions with $O(^3P)$.[40] More reactive molecules include halide ions, and those with oxidizable sulfur atoms or olefins.[16,40] As a result, the observed quantum yields are higher in cyclohexene than acetonitrile.

The strong luminescence and lack of deoxygenation from **2g** can be rationalized in at least two ways. First, the data are consistent with a case in which intersystem crossing to the luminescent triplet is very efficient and in which the photoreactivity of that state is very low. The blue-shifted emission spectrum of **2g**, relative to the other emissive sulfoxides, suggests that the triplet energy may be on par with or just below the S-O bond energy, but the carbonyl group may perturb the nature of the state more than the halogens. The lack of

structure in the spectrum suggests it is not a typical localized nπ* state of aromatic ketones such as benzophenone, but assignment beyond that is speculative. There is not a high correlation between phosphorescence yields and reactivity in another prototypical reaction of sulfoxides, photoinduced stereomutation, but the phosphorescence yields for compounds whose racemization have also been studied are all lower than for **2g**.[41-43] A second rationalization, also consistent with all the data, is that the introduction of the acetyl substituent and its attendant electronic influences directly perturbs the coupling between ISC and deoxygenation.

An alternative heavy atom strategy, which is reported separately, is the use of selenoxides instead of sulfoxides in a **DBTO**-like molecule.[44] In this case, the perturbation to the system is inherently greater because of changes in bond strength, bond lengths, aromaticity of the reduced compound, etc. However, the central location of the heavy atom at the key atomic position involved in the S-O (or Se-O) cleavage turned out to be a more dramatically successful strategy, in terms of producing a high quantum yield O-atom donor.

2.4 Conclusions

Halo-substituted dibenzothiophenes show a modest improvement in the quantum yield for deoxygenation, relative to the parent **DBTO**. The trend order of iodo > bromo > chloro ~ H allows assignment of this to a heavy atom effect. This is consistent with a proposed mechanism of unimolecular S-O scission in which bond stretching is coupled to intersystem crossing, presumably into the T_0 substate. From a quantitative point of view, the effect is smaller than that which would be optimum for demanding mechanistic studies of

$O(^3P)$ solution phase chemistry that require substantial concentrations of intermediates, such as flash photolysis.

2.5 Experimental Section

General

Reagents and solvents were used without further purification, except as noted. Dibenzothiophene was distilled under vacuum using a Kügelrohr apparatus at 175 °C. All MS data were obtained in EI (70 eV) or CI mode on a Finnigan TSQ 700 spectrometer.

Phosphorescence spectra were recorded at 77 K with an Edinburgh Instruments FL900 spectrometer, as reported previously.[17] The samples were contained in 5 mm suprasil cylindrical tubes within the Dewar. Fluorescence data were collected on a Spex FluoroMax instrument at ambient temperature with Ar-flushed samples that had an optical density of about 0.1 at the excitation wavelength, usually 265 nm.

Photolysis

All solvents were "spectro grade" or the equivalent and deoxygenated by sparging with argon bubbles for 10 minutes prior to photolysis. Cyclohexene was refluxed over Na under an Ar atmosphere and distilled immediately before use.

The initial concentrations of all photolysis experiments were in the range of 1.0 to 4.0 mM. Prior to photolysis, the samples were checked for purity using a HP 5890 II gas chromatograph equipped with ZB-5 capillary columns and a flame ionization detector. Dodecane was used as internal standard for all photolysis. Valerophenone was used as

actinometer for quantum yield measurements,[33] and samples were irradiated in 1 cm square cells.

Quantum yields were measured using a 75 W Xe arc lamp fitted to a monochromator set to 320 nm. The full output of the monochromator was absorbed by the samples, whose optical density at the excitation wavelength exceeded 2. Actinometry was repeated frequently to avoid any effect on quantum yield measurement due to any long-term drift in the light flux.

Preliminary photoreactions and some product analysis studies were done using a fan-cooled Rayonet mini-reactor at room temperature using broadly emitting 300 nm fluorescent tubes supplied by Southern New England Ultraviolet. The same reactor was used for the data shown in Figure 1, using both the 300 nm bulbs (RMR-3000) and 350 nm bulbs (RMR-3500).

Emission Spectra

Phosphorescence spectra were recorded at 77 K with an Edinburgh Instruments FL900 spectrometer, as reported previously.[17] The samples were contained in 5 mm suprasil cylindrical tubes within the Dewar. Fluorescence data were collected on a Spex FluoroMax instrument at ambient temperature with Ar-flushed samples that had an optical density of about 0.1 at the excitation wavelength, usually 265 nm.

4-Halo Dibenzothiophenes (1a-c)

4-Iododibenzothiophene and 4-chlorodibenzothiophene were prepared by the method of Katritzky.[23] 4-Bromodibenzothiophene was similarly prepared, save for the use of 1,2-

dibromoethane[45] as the electrophile. Dibenzothiophene (4g, 21.7 mmol) was dissolved in dry THF (40 mL). The solution was cooled to –40 °C. To this cold solution n-butyllithium (12 mL, 30 mmol) was added drop by drop. The mixture was gradually warmed to 0 °C and allowed to stir for 7 hours. Then it was again cooled to –40 °C and an appropriate nucleophile was added to it. For 4-iododibenzothiophene, iodine (12.4 g, 48.1 mmol) in dry THF and for 4-bromodibenzothiophene, 1,2-dibromoethane (4 mL, 45 mmol) in dry THF (6 mL) was added drop by drop. Lastly, for 4-cholordibenzothiophene *para*-tolylsulfonylchloride (5.18 g, 27.1 mmol) was added in the same way. For all three cases after the addition was over, the mixtures were allowed to warm to room temperature and were stirred for 15 hours. The products were isolated after routine work up method using saturated ammonium chloride. For 4-iodo-DBT the reaction mixture was also washed with sodium bisulfite solution to get rid of excess iodine from the reaction mixture. Some purifications were done by silica chromatography, using hexane as the eluent, rather than by recrystallization.

1a: Yield 95%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.17 (d, 1H, J = 7.6 Hz), 8.12-8.10 (m, 1H), 7.91-7.88 (m, 1H), 7.83 (d, 1H, J = 7.6 Hz), 7.52-7.50 (m, 2H), 7.22 (t, 1H, J = 7.6 Hz).

1b: Yield 85%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.15-8.12 (m, 1H), 8.13 (d, 1H, J = 0.9 Hz, 6.9 Hz), 7.92-7.89 (m, 1H), 7.63 (dd, 1H, J = 0.9 Hz, 7.5 Hz), 7.52-7.50 (m, 2H), 7.34 (t, 1H, J = 7.8 Hz).

1c: Yield 65%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.17-8.11 (m, 1H), 8.06 (dd. 1H, J = 1.2 Hz, 7.5 Hz), 7.93-7.89 (m, 1H), 7.55-7.49 (m, 2H), 7.47 (d, 1H, J = 1.2 Hz), 7.42 (t, 1H, 7.5 Hz).

2-Bromodibenzothiophene (1d)

2-Bromodibenzothiophene was prepared by the method of Shimomura.[46] Dibenzothiophene (4 g, 0.02 mol) was dissolved in chloroform (22.4 mL). Bromine (1.13 mL, 0.02 mol) was added dropwise at 0 °C with stirring. The reaction mixture was stirred at room temperature for 4 days. The reaction mixture was extracted with aqueous bicarbonate solution and the organic layer was evaporated. The crude product was sublimed thrice under reduced pressure, but compound **1d** could not be completely separated from the dibromo derivative **1e** (5% of the total mixture). The corresponding sulfoxides, however, were more rigorously purified. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.29 (d, 1H, J = 1.8 Hz), 8.12 (m, 1H), 7.87 (m, 1H), 7.73 (d, 1H, J = 8.4Hz), 7.55 (dd, 1H, J = 8.4, 1.8 Hz), 7.49 (m, 2H).

2,8-Dibromodibenzothiophene (1e)[26]

This compound was prepared by the method of Shimomura as for **1d**, with the modification that 2.8 equivalents of Br_2 was used. After purification by sublimation off of the **DBT** and **1d**, a 60% yield was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.24 (d, 2H, J = 1.8 Hz), 7.72 (d, 2H, J = 8.7 Hz), 7.59 (dd, 2H, J = 1.8 Hz, 8.7 Hz).

2,8-dichlorodibenzothiophene (1f)

This compound was prepared in low yield by the method of Savin,[25] whose original report on the reaction of dibenzothiophene with excess sulfuryl chloride suggests that the sulfoxide would be formed instead of the dichlorinated **DBT** derivative. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.09 (d, 2H, J =2.1 Hz), 7.77 (dd, 2H, J = 8.4 Hz, 0.6 Hz), 7.47 (d, 2H, J = 2.1 Hz). MS(CI) *m/z* 256/254/252 (M^+), 218, 181.

2-Acetyldibenzothiophene (1g)

2-Acetyldibenzothiophene was prepared by the method of Campaigne.[47] Partially pure 2-bromodibenzothiophene (0.80 g, 3 mmol) was dissolved in dry ether (20 mL). The mixture was stirred under argon atmosphere for half an hour and then *t*-butyllithium (2.25 equiv., 4.5 mL) was added cautiously to the solution and was stirred for another half an hour at –20 °C. To the lithiated DBT, was added *N,N*-dimethylacetamide (0.30 mL, 4 mmol) and stirred for half an hour at –20 °C. Then it was stirred for half an hour at room temperature, and refluxed for 20 minutes. A mixture of water (20 mL) and HCl (6 N, 3 mL) was added and the ether layer was separated. The aqueous phase was washed with ether (4 × 15 mL) and the combined extract was successively washed with sodium bicarbonate solution and water. The organic layer was evaporated and the product was purified using preparatory TLC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, 1H, J = 1.2 Hz), 8.26-8.24 (m, 1H), 8.05 (dd, 1H, J = 1.6 Hz, 8.0 Hz), 7.91 (d, 1H, J = 8.4 Hz), 7.89-7.87 (m, 1H), 7.53-7.51 (m, 2H), 2.74 (s, 3H).

Halodibenzothiophene oxides (2a-g)

Halodibenzothiophene or **1g** (1 equivalent) was dissolved in dichloromethane, typically 20 mL per g starting material, and was cooled to –30 °C. To this solution, *m*CPBA, dissolved in dichloromethane, was added dropwise over 30 min. The reaction was allowed to stir at this temperature until TLC indicated the appearance of sulfone, typically about 1 h. The mixture was then warmed to room temperature over a few minutes and quenched by addition of aqueous bicarbonate. After separation, drying, and evaporation of solvent, a white solid was obtained, and the sulfoxide was isolated by silica chromatography using 1:1 hexane/ethyl acetate as the eluent. Yields were typically 30 - 50%. Analytically pure samples were typically obtained by prep TLC.

4-Iododibenzothiophene-5-oxide (2a)

Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.88 (dd, 1H, J = 7.6 Hz, 0.8 Hz), 7.70 (dd, 1H, J = 8.0 Hz, 0.4 Hz), 7.68 (dd, 1H, J = 4.8 Hz, 0.8 Hz), 7.64 (dd, 1H, J = 8.0 Hz, 0.4 Hz), 7.50 (td, 1H, J = 7.6 Hz, 1.2 Hz), 7.42 (td, 1H, J = 7.6 Hz, 1.2 Hz), 7.16 (t, 1H, J = 7.6). ^{13}C NMR (400 MHz, $CDCl_3$): δ 148.3, 144.5, 139.4, 139.1, 136.9, 133.9, 132.8, 130.3, 127.7, 122.5, 121.7, 94.8. MS(EI) *m/z* 326 (M^+), 310, 171, 137.

4-Bromodibenzothiophene-5-oxide (2b)

Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ8.01(d, 1H, J = 7.6 Hz), 7.90-7.75 (m, 2H), 7.63 (td, 1H, J = 7.6 Hz, 1.2 Hz), 7.59 (dd, 1H, J = 8.2 Hz, 0.6 Hz), 7.55 (td, 1H, J = 7.6 Hz, 0.8 Hz), 7.46 (t, 1H, J = 7.6 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ 145.0, 144.7, 139.9,

136.8, 134.3, 133.2, 132.9, 130.4, 127.8, 123.4, 122.5, 120.9. MS(EI) *m/z* 280/278 (M^+), 264/262, 199, 171.

4-Chlorodibenzothiophene-5-oxide (2c)

Yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.84 (dq, 1H, J = 7.8 Hz, 0.6 Hz), 7.77 (dd, 1H, J = 7.5 Hz, 0.9 Hz), 7.72 (dd, 1H, J = 7.5 Hz, 0.9 Hz), 7.65 (td, 1H, J = 7.5 Hz, 1.2 Hz), 7.55 (m, 2H), 7.46 (t, 1H, J = 7.8 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ 138.0, 136.9, 134.9, 134.7, 134.3, 134.2, 131.1, 130.0, 122.5, 121.9, 120.5, 117.6. MS(EI) *m/z* 236/234 (M^+), 220/218, 199, 183.

2-Bromodibenzothiophene-5-oxide (2d)

Yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$): δ8.01 (dm, 1H, J = 7.8 Hz, 0.6 Hz), 7.96 (d, 1H, J = 1.8 Hz), 7.86 (d, 1H, J = 8.1 Hz), 7.79 (dm, 1H, J = 7.8 Hz, J = 0.6 Hz), 7.67-7.61 (m, 2H), 7.56 (td, 1H, J = 7.5 Hz, 1.2 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ 145.9, 144.1, 139.3, 136.1, 133.0, 132.6, 130.5, 129.0, 127.9, 127.6, 125.5, 122.4. MS(EI) *m/z* 280/278 (M^+), 264/262, 199, 183, 171, 139.

2,8-Dibromodibenzothiophene-5-oxide (2e)

Yield: 30%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ7.95 (d, 2H, J = 1.5 Hz), 7.87 (d, 2H, J =8.1 Hz), 7.68 (dd, 2H, J =1.8, Hz 8.1 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ144.5, 138.0, 133.4, 129.2, 127.8, 125.7. Mass (EI) *m/z* 360/358/356 (M^+), 344, 342, 340, 279, 277, 251, 249.

2,8-Dichlorodibenzothiophene-5-oxide (2f)

Yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.94 (d, 2H, J = 8.4 Hz), 7.78 (d, 2H, J = 1.8 Hz), 7.53 (d, 2H, J = 1.8 Hz, 8.1 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ139.7, 138.0, 130.4, 129.0, 122.7. (Note: This compound is very insoluble in most NMR solvents. Even overnight carbon NMR failed to show the one missing quaternary peak, i.e., the carbon adjacent to S. The missing peak should be in 140-145 ppm region.) MS(EI) *m/z* 270/268 (M^+), 254/252, 233.

2-Acetyldibenzothiophene-5-oxide (2g)

Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ8.41 (d, 1H, J = 1.2 Hz), 8.13-8.07 (m, 2H), 8.04 (d, 1H, J = 7.6 Hz), 7.94 (d, 1H, J = 7.6 Hz), 7.68 (t, 1H, J = 7.6 Hz), 7.58 (t, 1H, J = 7.6 Hz), 2.73 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ133.1, 130.4, 129.7, 128.0, 127.9, 122.6, 121.6, 27.3 (Quaternary carbons not given because of small scale of reaction.). MS(EI) *m/z* 242(M^+), 226, 211, 183.

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(31) See, for example, ref DAN GREGORY PAPER.

(32) The phosphorescence spectrum of 1g is considerably more structured and has a blue edge onset near 400 nm.

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CHAPTER III

PHOTOCHEMISTRY OF SUBSTITUTED DIBENZOTHIOPHENE OXIDES: THE EFFECT OF TRAPPING GROUPS

Based on a paper published in the *Journal of Organic Chemistry*[1]

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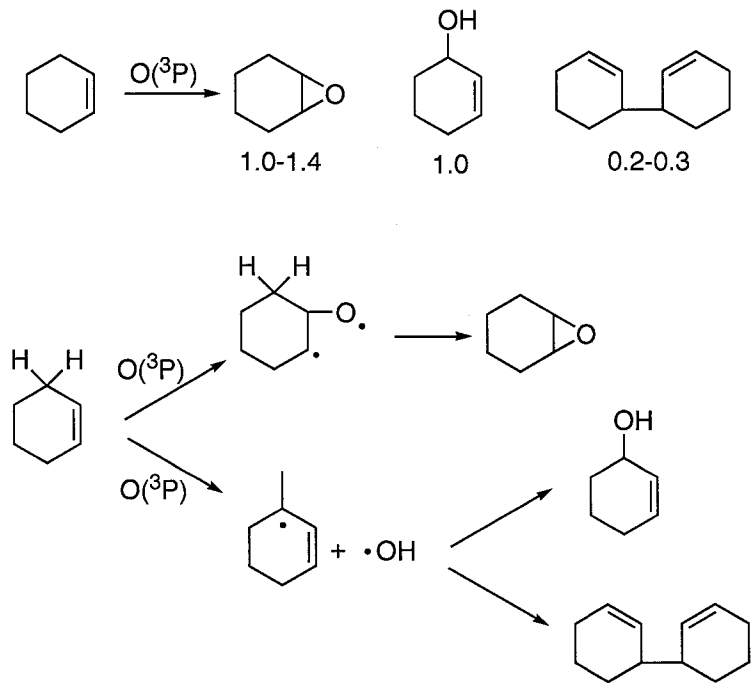
Abstract: Photolyses of dibenzothiophene sulfoxides (**DBTO**s) with intramolecular trapping functionalities attached in the 4-position show higher quantum yields of deoxygenation. Deoxygenation quantum yields are also less solvent dependent for the substituted **DBTO**s. Product analysis shows a detectable amount of intramolecular O-trapped products and suggests that solvent effects observed in previous studies of **DBTO** derive at least mainly from the reactivity between the oxidizing species that is released – presumably $O(^3P)$ – and the solvent, rather than from other macroscopic solvent parameters.

3.1 Introduction

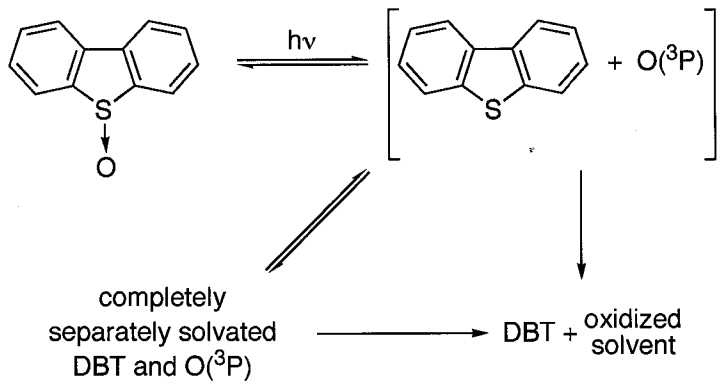
Along with C–S homolysis and stereomutation, one of the fundamental photochemical reactions of aromatic sulfoxides is deoxygenation to form the corresponding sulfide.[2-17] Direct photolysis of dibenzothiophene oxide (**DBTO**) provides a nearly quantitative yield of dibenzothiophene (**DBT**).[6,13,14] Mechanistic evidence strongly favors a unimolecular mechanism for deoxygenation, and several experiments point to formation of $O(^3P)$. For example, while direct evidence for formation of this active oxygen species is lacking, the oxidation pattern of various substrates is quite consistent with expectations for it.[8,9,13]

It has already been reported that the quantum yield of **DBT** formation is higher in tetrahydrothiophene, cyclohexene, and DMSO than in many other solvents.[13] The quantum yield of **DBT** formation in acetonitrile and benzene were 0.0026 and 0.0030 respectively. These two values are comparable but the quantum yield was much higher in cyclohexene (0.0100), tetrahydrothiophene (0.0085) and DMSO (0.0079). The detailed product analysis of the oxidized cyclohexene was done extensively by Gregory and coworkers[18] and they are shown in Scheme 2. The proposed mechanism for the formation of three different oxidized products is also shown. Although it is not stated clearly about the oxidation product of tetrahydrothiophene solvent, it is most likely that it forms sulfoxide.



Scheme 1. Oxidation of cyclohexene by $O(^3P)$ and its mechanism

The higher quantum yield in cyclohexene, tetrahydrothiophene and DMSO can be explained by supposing that these three were better oxygen atom acceptors than other solvents (e.g., THF, isopropyl alcohol) and that the nascent sulfide (**DBT**) competes with the solvent as an acceptor of the oxygen atom, as shown in Scheme 2. It would be expected that these solvents, which react most rapidly with $O(^3P)$ – would produce net deoxygenation quantum yields closer to the quantum yield of the initial cleavage event itself, though the latter number has not been established.



Scheme 2. The quantum yield of **DBTO** deoxygenation is higher when the solvent competes more effectively for the oxygen atom

This explanation points to a new series of experiments. Substituents can be appended to the 4-position of **DBTO** that should themselves act as chemical traps for $O(^3P)$ without affecting the bulk solvent parameters such as polarity or hydrogen bonding capability. A **DBTO** derivative with an appropriate functionality could yield the internally trapped products and be considerably less sensitive to solvent effects. A higher overall quantum yield might be expected for such a molecule (than is observed for **DBTO)** in solvents that are among the low group for **DBTO** itself, e.g., acetonitrile. The identity of the functional group is obviously of key importance. However, it should also be expected that the chain length between the trapping functionality and the **DBTO** nucleus will affect the efficiency of trapping and the relative effect of solvent on the observed quantum yields.

The most straightforward choices for trapping functionalities are alkenes and sulfides. These derive from the solvents that had higher quantum yields in our previous work,[13] and the molecules had very high rate constants in a kinetic study of Bucher and Scaiano.[19,20] We now report the preparation and photochemistry of sulfoxides **1a–c** and **2a–d** (Chart 1), and

show that their photochemistry supports the hypothesis laid out in Scheme 2, though the results are more complex than most simply implied by the above analysis.

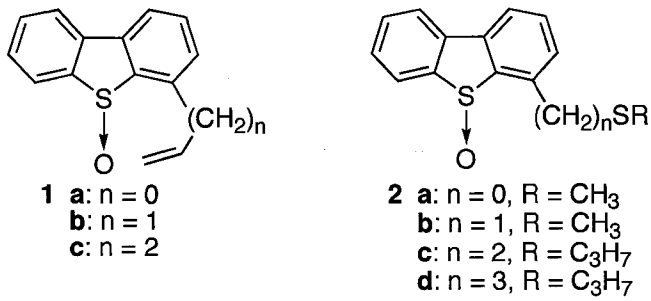
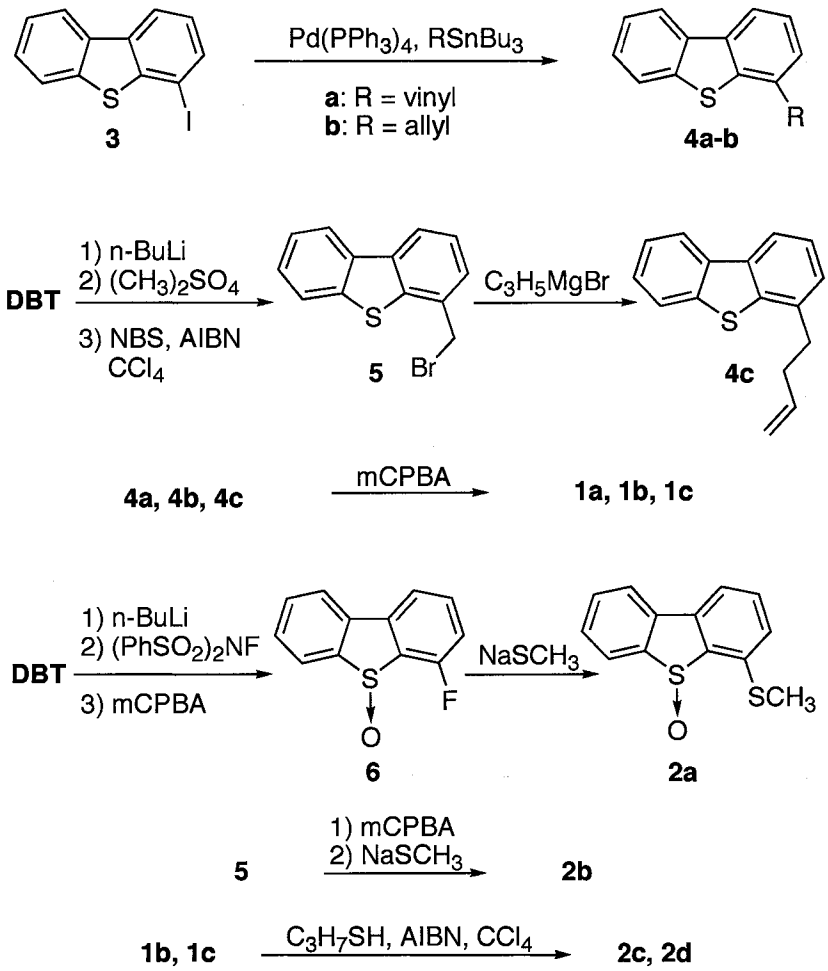


Chart 1. Substituted **DBT** and **DBTOs**

3.2 Results

Preparation of Sulfoxides 1a–c and 2a–d

The preparations of the sulfoxides are outlined in Scheme 3, while full synthetic details are given in the Experimental section. 4-Iododibenzothiophene[21] was converted to the corresponding vinyl or allyl **DBT** derivative via Stille coupling.[22-26] This was followed by selective oxidation of the sulfur using mCPBA.[27,28] For preparation of **1c**, methylation in the 4-position was followed by benzylic bromination.[29,30] An allyl group was then coupled by way of Grignard chemistry,[31] and oxidation was carried out.[28]



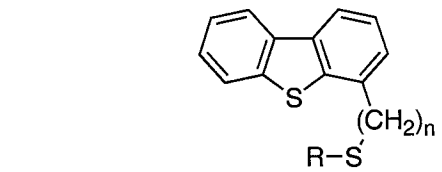
Scheme 3. Preparation of sulfoxides

DBTO derivatives with a sulfide appendage could not be prepared from the corresponding precursors **7** with oxidation as the final step because the oxidation of **DBT** is sluggish relative to that of other sulfides. Instead, the functionality must be introduced to the preoxidized **DBTO** derivative. Sulfoxide **2a** was prepared by nucleophilic substitution of the corresponding fluoro-substituted **DBTO 6**.[32] Sulfoxide **2b** was prepared via intermediate **5** by oxidation and substitution. Compounds **2c** and **2d** were prepared with SC_3H_7 groups, rather than SCH_3 because the method of preparation involved radical addition of the thiol to

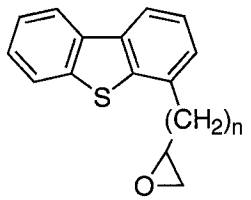
the corresponding sulfoxides **1b** and **1c**.[33] The propyl group served to make the thiol easier to handle than methanethiol.

Photoproducts

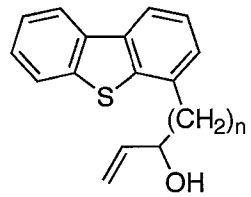
The method of choice for identification and quantification of products in this study was GC-MS. It was anticipated that compounds **1a–c** might, respectively, produce epoxides **8a–c** and/or allylic alcohols **9b, c** or **10b, c** as intramolecular trapping products (Chart 2).[13,34] Preliminary photolyses of **1b** gave GC-MS peaks that had the same mass as **1b** but different retention times, consistent with this idea. As such, it was desirable to prepare the potential photoproducts independently for comparison of their chromatographic and mass spectral behavior.



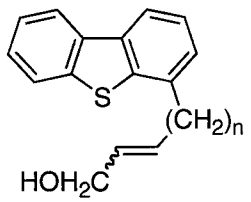
7a: n = 0, R = CH_3
b: n = 1, R = CH_3
c: n = 2, R = C_3H_7
d: n = 3, R = C_3H_7



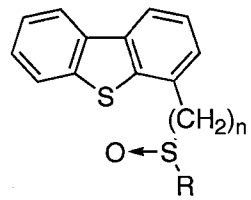
8a: n = 0
b: n = 1
c: n = 2
d: n = 3



9b: n = 0
c: n = 1



10b: n = 0
c: n = 1



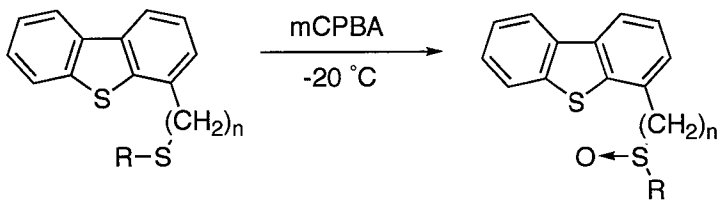
11a: n = 0, R = CH_3
b: n = 1, R = CH_3
c: n = 2, R = C_3H_7
d: n = 3, R = C_3H_7

Chart 2. Structures of **DBT**s, **DBTO**s and internally trapped products

Attempts to produce products **8b–d**, however, were not successful. For example, the preparation of **8b** was attempted by the coupling of 4-lithiodibenzothiophene to epichlorohydrin using CuCN as a catalyst[35] and by dihydroxylation[36] of **4b**, which would eventually give **8b** by dehydrative ring closure; neither of these pathways were fruitful. Instead, then, for compounds **8–10**, assignments of GC-MS peaks to structures were based on the fragmentation patterns observed in the EI mass spectra, which were compared to functional group analogues using benzene as the aromatic nucleus instead of

dibenzothiophene. (For example, styrene oxide was used as the analogue of **8a**.) In contrast to the internally trapped products from **1a-c**, deoxygenated sulfides **4a-c** were already available from the preparation of the sulfoxides.

The potential photoproducts from **2a–d** were straightforward to prepare. Deoxygenated sulfoxides **7a–d** were obtained by routes analogous to the preparations of **2a–d**, save that the dibenzothiophene nucleus was not oxidized. Sulfoxides **11a–d** were then obtained by oxidation of the compounds in the **7** series. As mentioned before aryl alkyl and dialkyl sulfides can be easily oxidized than diaryl sulfides, it was possible to prepare sulfoxides **11-d** from **7a-d** at low temperature.



7a: n = 0, R = CH_3
b: n = 1, R = CH_3
c: n = 2, R = C_3H_7
d: n = 3, R = C_3H_7

11a: n = 0, R = CH_3
b: n = 1, R = CH_3
c: n = 2, R = C_3H_7
d: n = 3, R = C_3H_7

Scheme 4. Preparation of sulfoxides **11a-d**

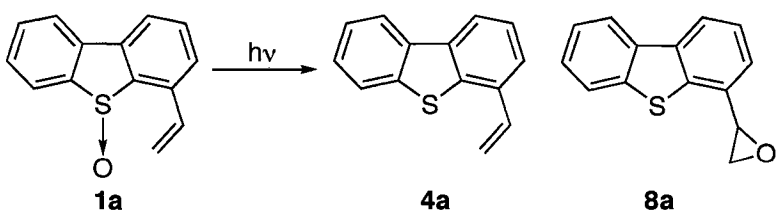
General Photolysis Conditions

Photolyses of compounds **1** and **2** were done in Ar-flushed solvents using a Xe-arc lamp coupled to a monochromator set to 320 nm (± 12 nm linear dispersion), which is near the first absorption maxima of these compound. Initial concentrations were in the range of 5 mM. Product distributions and quantum yields are quoted at low conversion (ca. 10%) unless otherwise noted. All solvents were spectro-grade when available. Cyclohexene was

refluxed under Ar over Na for several hours and then distilled immediately before use. Photolyses carried out in cyclohexene (only) were done after 3–5 freeze-pump-thaw cycles in addition to the Ar flushing to eliminate as much O_2 as possible. All quantum yields were measured using valerophenone as an actinometer.[37]

Photolysis of Olefin-Labeled Sulfoxides 1a–c

Photolysis of 4-vinyl **DBTO 1a** to low conversion in acetonitrile provided only the deoxygenated product **4a** in apparently quantitative yield. In benzene, the sulfur-containing products were a mixture of **4a** and epoxide **8a** in a 3:1 ratio, again in quantitative yield with respect to consumed starting material. The assignment of the new product to **8a** was based on a comparison of its EI-MS fragmentation pattern to those of styrene oxide, acetophenone, and phenylacetaldehyde, i.e., the benzene analogues of the reasonable side chain-oxidized isomers of **1a** (Scheme 5). The major peaks in the observed spectra were $(M - 17)^+$, $(M - 31)^+$, and $(M - 43)^+$, which corresponded well to styrene oxide; the other compounds had much different fragmentation patterns. The quantum yields for deoxygenation in these two solvents are both near 0.002, as reported in Table 1.



1a **4a** **8a**

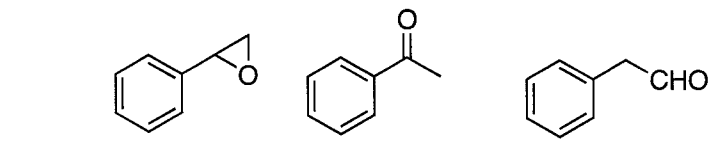
Scheme 5. Photolysis of 4-vinyl DBTO

Table 1. Results of photolysis of **1a-c** and **2a-d** in several solvents

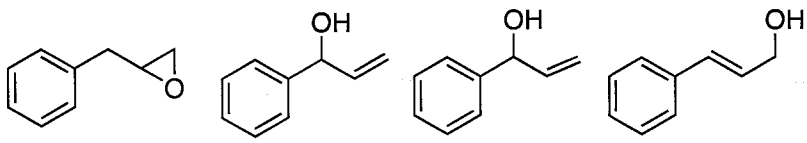
Compound	Solvent	Product(s)	Φ_{total}
DBTO[a]	acetonitrile	**DBT**	0.0026
	benzene	**DBT**	0.0029
	cyclohexene	**DBT**	0.0100
	DMSO	**DBT**	0.0079
1a	acetonitrile	**4a**	0.0018
	benzene	**4a** (75%), **8a** (25%)	0.0020
	cyclohexene	**4a**	0.010
1b	acetonitrile	**4b** (85%), **8b** (15%)	0.0074
	benzene	**4b** (75%), **8b** (25%)	0.0068
	cyclohexene	**4b**	0.0126
	DMSO	**4b**	0.0078
1c	acetonitrile	**4c**	0.0085
	benzene	**4c** (75%), **8c** (25%)	0.0096
2a	acetonitrile	**7a**	0.0038
	benzene	**7a** (55%), **11a** (45%)	0.0058
	cyclohexene	**7a**	0.0114
2b[b]	acetonitrile	**7b** and **12**[b]	0.0048
2c	acetonitrile	**7c**	0.0028
	benzene	**7c**	0.0050
2d[c]	acetonitrile	–	~0

[a]Literature value.[13] [b]Secondary photolysis of **7b** leads to **12**. The reported quantum yield has a larger error associated with it, because it is only to about 3% conversion, to avoid excessive secondary photolysis. [c]Extended photolysis did not lead to observable photochemical reaction.

Photolysis of **1b** and **1c** gave similar results. The allyl sulfoxide yielded mainly the deoxygenation product **4b**, with 15 and 25% yields of **8b** in acetonitrile and benzene, respectively. Homoallyl-substituted sulfoxide **1c** did not provide detectable **8c** in acetonitrile, but provided both the deoxygenation (**4c**) and trapped product (**8c**) in benzene, as shown in Table 1. Quantum yields are higher for both of these compounds. Again, the assignments of the structures of the observed GC-MS peaks to **8b** and **8c** were done by comparison of the fragmentation to the benzene analogues of structures **8** – **10**. In chart 3 examples of the benzene analogues for the possible trapped products that could form in the photolysis of **1a** and **1b** are shown. The comparison shows that the trapped products formed in both cases have similar fragmentation pattern in GC-MS to the first compounds in both the sets, i.e. the epoxide.



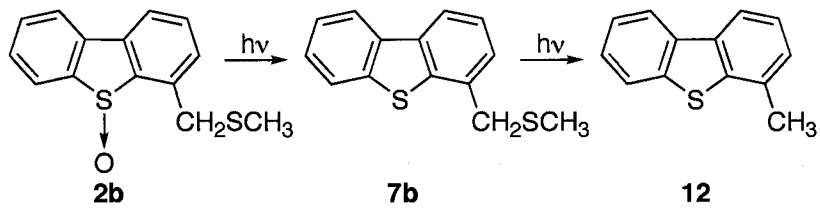
Set 1: Compared to the possible internally trapped product formed in the photolysis of **1a**



Set 2: Compared to the possible intrnally trapped product formed in the photolysis of **1b**

Chart 3. Benzene analogues of the trapped products **8-10**

The results among the thio-substituted **DBTO**s were less uniform. Sulfoxide **2a** behaved largely as the olefins had. An apparently quantitative yield of **7a** was obtained in acetonitrile, while a 55:45 mixture of **7a** and **11a** was obtained in acetonitrile. Compound **2b**, however, had a more complex behavior. In acetonitrile, at low conversion (ca. 10%), a 2:1 mixture of **7b** and 4-methyldibenzothiophene **12** was observed. As the reaction proceeded, the ratio dropped until all the **7b** was converted to **12**. The apparent explanation that photolysis of **7b** yields a benzylic-type homolysis reaction that gives **12** was confirmed by independent photolysis of **7b** (Scheme 6). The quoted quantum yield (Table 1) of 0.0048 is subject to a greater error than the others because we attempted to extrapolate the data more closely to zero conversion to get around the secondary photolysis problem.



Scheme 6. Secondary photolysis of **2b**

We cannot rule out that a certain amount of **12** is produced on direct photolysis of **2b** but do not believe this to be the case. We also cannot rule out that photolysis of **2b** produces some of the internally trapped sulfoxide **11b**, which in turn is photolyzed to **12** in high quantum yield, but **11b** was not ever detected in any of the reaction mixtures.

Photolysis of **2c** resulted only in formation of **7c**, with a quantum yield of 0.0050 or 0.0028, depending on the solvent. Photolyses of **2d** were carried out in benzene and

acetonitrile. In neither solvent was any new product observed; the starting material remained unchanged.

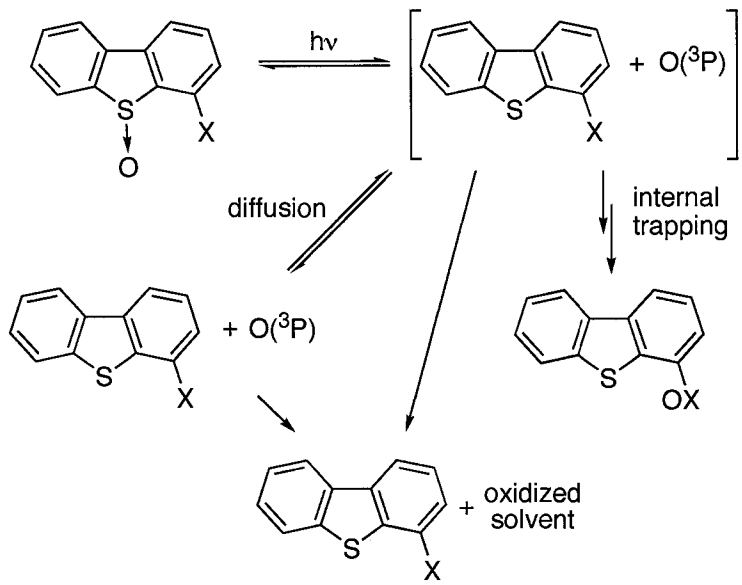
As reported in Table 1, **1a**, **1b**, and **2a** were also photolyzed in cyclohexene. These were the starting materials that showed significant internal trapping products in the other solvents. In each case, the only sulfur-containing product was that of deoxygenation, i.e., **4a**, **4b**, and **7a**, respectively. Also, the samples were checked for oxidized solvent products. Cyclohexene oxide and 2-cyclohexenol were observed in ratios of 1:2, 1:2, and 1:1.4 for the three cases.

3.3 Discussion

In our 1997 paper on the photodeoxygenation of **DBTO**, we reported the quantum yield obtained with 320 nm irradiation for deoxygenation in 13 solvents. The value was 0.0030 ± 0.0004 for the great majority of these: acetonitrile, benzene, 2-propanol, tetrahydrofuran, toluene, and four different alkane solvents. Only cyclohexene, DMSO, and tetrahydrothiophene, stood out, with values of 0.0100, 0.0079, and 0.0085, respectively. For purposes of further discussion, we will refer to these two sets as the "low quantum yield solvents" and the "high quantum yield solvents," respectively.

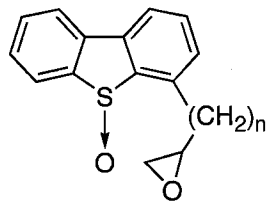
Given the structural diversity of the solvents in both groups, we asserted that the variation in quantum yield had mainly to do with specific functionality of the high quantum yield solvents, rather than a bulk property such as polarity.[13] As implied in Scheme 2, those solvents that reacted with $O(^3P)$ more rapidly than the others showed a higher quantum yield because of the competitive back-reaction of the oxygen atom with **DBT**. The experiments here address this attribution by expanding this notion to that in Scheme 4, where the explicit

functionality in the pendant group X is designed to model that of the high quantum yield solvent. Then the substrate can be examined in multiple solvents, both among the high and low quantum yield groups. The effect of its X group and the concomitant high "effective local concentration" of what we pose to be the trapping functionality can be examined. In the event, it turns out that the results do not lead to a black and white conclusion, but we believe that we may draw speculative interpretations that are consistent with Scheme 7 and the explanation of the solvent effect that we advanced previously.



Scheme 7. An expanded reaction scheme, accounting for internal trapping by the pendant functionality

We first consider the results for the series **1a-c** with Scheme 4 in mind. In none of the experiments was a product observed, such as **13**, which corresponds to an *intermolecular* trapping product from **1a**. Because of the lack of any such "M + 16" product in all the photolyses, we assume that all the trapped products come from unimolecular chemistry.



13

It is immediately notable that the quantum yields for deoxygenation for compounds **1b** and **1c** are in the range that would have been in (or at least quite near) the "high quantum yield solvent" group for **DBTO**. These are also two cases in which internally trapped products are observed, consistent with the hypothesis in Scheme 7. When the photolyses are carried out in the most efficient externally trapping solvent, i.e., cyclohexene, the quantum yield is near 0.01 for both of them. This value is still higher than the quantum yield in benzene or acetonitrile, and the internally trapped products disappear. This is entirely consistent with the idea that the principal quality of cyclohexene that makes it a "high quantum yield solvent" is its ability to trap the nascent $O(^3P)$. It also suggests that 0.01 is near the quantum yield limit that would be obtained for 100% trapping of the oxygen atom for **DBTO** derivatives whose substituents do not have a substantial effect on the excited states or their dynamics.

It is, however, considerably less obvious why no internally trapped product is observed for **1a** and **1c** when photolysis is carried out in acetonitrile. According to Scaiano's data,[19] $O(^3P)$ reacts about 300 times more rapidly with benzene than with acetonitrile. (It is thought that the major reaction channel in acetonitrile is formation of the nitrile oxide, but we did not specifically examine any of the reaction mixtures for products of solvent oxidation.)

Thus, one might expect that a greater fraction of the photolyzed material might be expected to end up as the internally trapped product in CH_3CN. It may be speculated that the lower viscosity acetonitrile might be more conducive to diffusive separation of $O(^3P)$ from the **DBT** derivative; however, this should lead to a greater quantum yield for **DBTO** as well, and this is not observed.

However, the greater polarity of acetonitrile might also be more conducive to separation of O from the **DBT** nucleus if the pathway to their formation involves significant charge separation. Greer has made the argument that charge separation is involved in the related (and also spin-forbidden) oxidation of sulfides by $O(^3P)$ in solution[8,9] and it has been widely noted that there is a correlation between substrates' low ionization potential and high gas phase reaction rate constants with $O(^3P)$.[38-43] Though not strictly a case of microscopic reversibility, it is reasonable to infer that the same charge separation may also occur as S-O dissociation begins on an excited state energy surface. (The logical limit of a mechanism along these lines involves **DBTO*** forming a transient ion pair **DBT**$^{\bullet+}$/$O^{\bullet-}$, which forms **DBT** and $O(^3P)$ by back electron transfer.) This "looser" transition state in acetonitrile might easily lead to lower trapping efficiency for entropic reasons.

A second point in this series about which we can only speculate is the data set for **1a**, a compound that shows trapping products in benzene but not an elevated Φ. The observed quantum yield for **1a**, approximately 0.002 regardless of the solvent, is lower than that for the other two in the series and is comparable to that of **DBTO**. Here, we speculate in hindsight that the direct attachment of the vinyl group to the aromatic ring provides unpredictable results on the basis of the possibility of cis-trans isomerization as a mechanism for excited state deactivation. In retrospect, it could easily have been the case that the vinyl group

coupled to the aromatic moiety of **DBTO** in such a way as to completely eliminate the deoxygenation process; in any case, the vinyl substituent should decrease the observed deoxygenation quantum yield because of this to some degree. That the *cis-trans* isomerization deactivation is relatively *in*efficient is evidenced both by the observation of the internally trapped products in benzene and the observation of a quantum yield of 0.01 in cyclohexene. Nonetheless, this issue does muddy the comparison of **1a** to **DBTO** and the rest of the series.

The series of compounds with sulfanyl labels **2a**–**2d** behaves less uniformly than does the series **1a-1c**, but the "misbehavior" is straightforward to rationalize. Again, none of the quantum yields qualitatively exceeds 0.01, consistent with this being the approximate upper limit for a conventional **DBTO** nucleus. Trapping products are observed for **2a** in benzene but not in acetonitrile, as mentioned above. With a CH_2SCH_3 appendage, no trapping products were observed in acetonitrile, but secondary photolysis led to methyl-substituted dibenzothiophene **12**. As a result of this complication, we chose not to pursue the photolysis of this compound extensively. When the facile benzylic homolysis is removed by homologation to **2c**, still no trapping products are observed, and the quantum yields are comparable to those for **DBTO**. This simply implies that the best geometry for internal trapping before dissociation (including the unfavorable entropic issues involved with the flexible linker) is best achieved with compound **2a**.

The simplest interpretation of these data for the photoinert **2d** is that the pendant sulfide is poised at a particular length that quenches the reactive excited state much more efficiently than the other analogues. This idea has precedent, for example, in β–phenylvalerophenone, which is a uniquely unreactive phenyl ketone toward internal

hydrogen abstraction.[44] In analogy to that example, the mechanism for quenching by the side chain of **2d** is most likely reversible charge transfer from the side chain sulfur to the easily reduced[45] **DBTO** nucleus.

An alternative interpretive framework with substantial merit has been offered by a referee. It was suggested that the initially populated excited state, rather than "bifurcating" into a reactive channel that generates $O(^3P)$ and one or more nonreactive channels (e.g., formation of the low-energy T_1 state), undergoes a "trifurcation." In addition to the two channels described previously, it is hypothesized that a particular excited state, perhaps T_2, acts as a second oxygen transfer agent if an appropriate receptor is available. Under this framework, the quantum yield of $O(^3P)$ formation is universally about 0.003, and the maximum additional oxygen transfer quantum yield is about 0.007. It is entirely reasonable to suggest that such a mechanism, which would not entail any diffusible intermediates, would have a distinct dependence on the chain lengths between the S-O bond and the trapping functionality because of a limited range of transition state geometries that could effect the oxygen transfer. The fact that trapped products are favored in benzene, relative to acetonitrile, would then depend on a differential solvent effect on the two channels that did not affect the total reaction quantum yield much, but did deflect more of the compound to the $O(^3P)$ channel. The same basic arguments we presented above in favor of $O(^3P)$ formation could be invoked here.

In our 1997 paper,[13] we reported that the quantum yield of **DBTO** deoxygenation is dependent on the wavelength of irradiation such that irradiation into S_2, rather than S_1, increased the deoxygenation efficiency. This clearly indicates that there are multiple channels of reactivity, i.e., reactivity out of S_1 and some other excited state such as an upper

triplet or upper singlet. While this observation is clearly consistent with the hypothesis that an upper excited state might react as a direct oxygen transfer reagent, while the other reacts as an $O(^3P)$ donor, it is also consistent with two states leading to the common diffusible intermediate with different quantum yields. We thus cannot distinguish between the two hypotheses on the basis of the current data.

However, one thing we will address in a separate publication is the possibility that the two hypotheses could be distinguished by an "oxidation fingerprinting" method, as was used to argue that dibenzoselenophene-*Se*-oxide and **DBTO** produce a common oxidizing species.[46] The two different oxidizing species postulated above ought to show different selectivities among substrates. This same approach is being taken for a study of various sensitized **DBTO** deoxygenations, and a report that will include an exploration of the wavelength effect will be forthcoming from these laboratories.

3.4 Conclusion

Ultimately, while the results of this study are not entirely satisfying, they are at least consistent with the hypothesis advanced, that it is largely the specific functionality of some of the solvents that leads to more efficient photochemical deoxygenation, rather than other macroscopic parameters. However, the results also reduce what might usually be the "conclusions" of a work to "interpretations".

The members of the two series were chosen on the basis of the unpredictability of how many methylenes would be ideal for trapping. Assuming the basic hypothesis was correct, there was the expectation that there might be some sort of smooth curve of results in which the efficiency of internal trapping would be maximized at a particular chain length.

We suggest that the behaviors of **1a**, **2b**, and **2d**, are "exceptional" because of the unintended alternate reactivity induced by their functionalities. For overall trapping efficiency, it is **1b** that comes out ahead among the olefin series and **2a** among the sulfanyl series. The alternate reactivity of **2b** due to benzylic-type cleavage doomed this compound from the ability to show whether the additional methylene would increase trapping efficiency in that series.

Furthermore, on the basis of the internal trapping effects, our initial assumption that benzene and acetonitrile would be effectively identical solvents for deoxygenation appears to have been false. Again, this can be interpreted in reasonable terms, i.e., that the transition state for deoxygenation involves some charge separation that acetonitrile can help solvate, but proof awaits further work. An alternative hypothesis that involves multiple excited states and at least two distinct mechanisms of deoxygenation also cannot be eliminated. Experimental and computational efforts are underway to address these and related issues.

3.5 Experimental Section

General

Routine gas chromatography and quantification was performed on an instrument with a flame ionization detector, and it was assumed that the response factors for isomeric compounds would be identical. GC-MS analyses were done with either an EI/CI-quadruple MS or a benchtop instrument with an ion trap. All analyses were done using a 30 m 5% phenyl column. Reagents and solvents were used without further purification, except as noted. Dibenzothiophene was distilled under vacuum using a Kügelrohr apparatus at 175 °C. All MS data were obtained in EI (70 eV) or CI mode on a Finnigan TSQ 700 spectrometer. All NMR spectra were taken in $CDCl_3$. Mass spectra were taken using EI mode, unless

otherwise noted. 4-Methyldibenzothiophene was prepared from **DBT** using a known procedure used by Katritzky.[47]

Photolyses

Experiments were carried out closely following previous procedures.[13] Photolyses were done in spectro grade solvents, as indicated with initial concentrations in the range of 1 – 5 mM. Cyclohexene was treated by refluxing under Ar and over Na immediately before use. Dodecane was used as internal standard for all photoreactions. Valerophenone was used as actinometer for quantum yield measurements. Irradiations were carried out with a 75 Xe arc lamp from PTI, coupled to a matching monochromator. All the settings of the monochromator were kept constant during the measurements. Actinometry was repeated frequently to avoid any effect on quantum yield measurement due to any drift of the light flux. Some preliminary reactions were done using a Southern New England Ultraviolet Rayonet mini-reactor with broadly emitting 300 nm fluorescent tubes.

4-Vinyldibenzothiophene (4a) and 4-allyldibenzothiophene (4b)

4-Iododibenzothiophene[21] (50 mg, 0.16 mmol) was dissolved in dry benzene (3 mL). To this was added tetrakis(triphenylphosphine)palladium (18 mg, 0.016 mmol) and vinyltributylstannane (61.3 mg, 0.193 mmol) or allyltributylstannane (60.9 mg, 0.192 mmol). The reaction mixture was allowed to stir at reflux for about 24 hours under Ar. The reaction mixture was cooled and washed with saturated ammonium fluoride solution, followed by water and brine. The organic layer was evaporated and dried. The crude products were

purified using preparatory TLC (hexane). The isolated yields of the 4-vinyl and 4-allyl derivatives were both about 55%.

4a: ^{1}H NMR (400 MHz): δ 8.19-8.17 (m, 2H), 8.1 (d, 1H, J = 7.6 Hz), 7.92-7.88 (m, 1H), 7.59 (d, 1H, J = 7.6 Hz), 7.51-7.47 (m, 1H), 7.03 (dd, 1H, J = 17.6 Hz, 11.2 Hz), 6.02 (d, 1H, J = 17.6 Hz), 5.57 (d, 1H, J = 11.2 Hz). ^{13}C NMR (300 MHz): δ 145.0, 138.8, 136.4, 135.7, 135.1, 132.7, 127.0, 125.0, 124.68, 124.66, 122.9, 121.9, 121.0, 116.9. MS(EI) *m/z* 211, 210 (M+), 209, 183.

4b: ^{1}H NMR (300 MHz): δ 8.18-8.13 (m, 1H), 8.06 (d, 1H, J = 7.8 Hz), 7.90-7.86 (m, 1H), 7.50-7.45 (m, 2H), 7.45 (t, 1H, J = 7.2 Hz), 7.32 (d, 1H, J = 7.5 Hz), 6.25-6.01 (m, 1H), 5.23 (dq, 1H, J = 1.5 Hz, 16.8 Hz), 5.19 (dq, 1H, J = 1.5 Hz, 9.9 Hz), 3.67 (d, 2H, J = 6.3 Hz). ^{13}C NMR (400 MHz): δ 146.1, 144.5, 143.5, 140.1, 135.1, 134.3, 126.8, 126.6, 125.1, 124.6, 123.0, 121.9, 119.8, 117.3, 39.6. MS(EI) *m/z* 224 (M+), 208.

4-Homoallyldibenzothiophene (4c)

To a solution of allylmagnesium bromide (0.42 mL, 1 M in ether, 0.42 mmol) held at about 0 °C was added a solution of 4-bromomethyldibenzothiophene (5.57 mg, 0.21 mmol) in 3 mL ether. The mixture was allowed to warm to room temperature and stirred for 2 days under argon. Saturated ammonium chloride solution was added to quench the reaction. Then it was washed with water and brine, dried over magnesium sulfate, and the solvent was removed. Purification was by prep TLC (hexane) to give 4c in 55% yield. ^{1}H NMR (400 MHz): δ 8.18-8.14 (m, 1H), 8.04 (d, 1H, J = 7.6 Hz), 7.91-7.88 (m, 1H), 7.49-7.45 (m, 2H),

7.44 (t, 1H, J = 7.6 Hz), 7.31 (d, 1H, J = 7.6 Hz). 5.95 (q of t, 1H, J = 3.2 Hz, 10.4 Hz), 5.12 (d of q, 1H, J = 1.6 Hz, 17.2 Hz), 5.02 (dd, 1H, J = 1.6 Hz, 10.4 Hz), 3.02 (t, 2H, J = 7.6 Hz), 2.59 (q of d, 2H, J = 1.2 Hz, 8 Hz). ^{13}C NMR (400 MHz): δ 139.3, 139.2, 137.9, 136.3, 136.2, 135.8, 126.8, 126.4, 124.9, 124.5, 123.0, 121.9, 119.6, 115.5, 34.8, 33.3. MS(EI) *m/z* 238 (M+), 197.

General procedure for making DBTOs by oxidation of the corresponding sulfide

The sulfide (approximately 100 mg) was dissolved in dichloromethane (20 mL) and was cooled to –30 °C. To this solution, *m*CPBA (1 eq) in about 5 mL dichloromethane was added dropwise over a period of half an hour. After the addition, the mixture was allowed to stir for one hour at –30 °C, before being gradually warmed to room temperature. TLC was checked to monitor the reaction. The reaction stopped when the sulfone spot started showing up, which was generally about 1 h after addition was completed. To quench, the solution was washed with saturated sodium bicarbonate solution, and dried with MgSO4, following which the solvent was removed using a rotary evaporator to give a solid white product. The product was purified using preparatory TLC (1:1 hexane/ethyl acetate).

4-Vinyldibenzothiophene oxide (1a): Yield 40%. ^{1}H NMR (300 MHz): δ 7.96 (d, 1H, J = 7.5 Hz), 7.75 (d, 1H, J = 7.5 Hz), 7.66 (dd, 1H, J = 1.2 Hz, 7.5 Hz), 7.60-7.45 (m, 4H), 7.54(dd,1H), 7.39 (dd, 1H, J = 11.1 Hz, 17.4 Hz), 6.03 (d, 1H, J = 17.4 Hz), 5.64 (d, 1H, J= 11.1 Hz). ^{13}C NMR (300 MHz): δ 144.6, 142.0, 138.6, 137.7, 133.0, 132.6, 131.8, 129.7, 127.5, 126.1, 122.1, 121.1, 119.5. MS(EI) *m/z* 226 (M+), 210.

4-Allyldibenzothiophene oxide (1b): Yield 60%. ^{1}H NMR (400MHz): δ 7.99 (d of q, 1H, J = 0.4 Hz, 7.6 Hz), 7.80 (d of q, 1H, J = 0.4 Hz, 7.6 Hz), 7.68 (dd, 1H, J = 1.2 Hz, 8.0 Hz), 7.60 (td, 1H, J = 1.2 Hz, 7.6 Hz), 7.54 (t, 1H, J = 7.6 Hz), 7.50 (td, 1H, J = 1.2 Hz, 7.6 Hz), 7.29 (dd, 1H, J = 0.4 Hz, 7.6 Hz), 6.13-6.03 (m. 1H), 5.36 (dq, 1H, J = 1.6 Hz, 17.6 Hz), 5.21 (dq, 1H,1.2 Hz, 10.0 Hz), 3.98 (dd, 1H, J = 7.2 Hz, 15.6 Hz), 3.81 (dd, 1H, J = 6.4 Hz, 15.6 Hz). ^{13}C NMR (400 MHz): δ 144.9, 143.2, 141.6, 137.7, 137.4, 135.2, 133.1, 132.6, 130.4, 129.7, 127.6, 122.1, 120.1, 117.8, 37.0. MS(EI) *m/z* 240 (M+), 224/223.

4-(3-butenyl)dibenzothiophene oxide (1c): Yield 45%. ^{1}H NMR (300 MHz): δ 7.99 (d of q, 1H, J = 0.6 Hz, 6.9 Hz), 7.80 (dd, 1H, J=0.6 Hz , 7.8 Hz), 7.66 (dd, 1H, J = 0.6 Hz, 7.5 Hz), 7.6 (t of d, 1H, J = 1.2 Hz, 7.5 Hz), 7.53 (t, 1H. J = 7.5 Hz), 7.50 (t of d, 1H, J = 7.5 Hz), 7.29 (d, 1H, J = 7.5 Hz), 5.93 (q of t, 1H, J = 6.6 Hz, 10.2 Hz), 5.11 (m, 1H), 5.04 (m, 1H), 3.21 (m, 2H), 2.61 (m, 2H). ^{13}C NMR (400 MHz): δ 140.9, 138.3, 138.1, 133.9, 133.8, 132.1, 131.8, 131.4, 130.4, 122.2, 121.6, 119.5, 119.2, 115.4, 33.6, 30.9. MS(EI) *m/z* 254 (M+), 237.

4-Fluorodibenzothiophene oxide (6)

4-Fluorodibenzothiophene was first prepared by adaptation of a literature method.[48] To a cold (-50 °C) solution of **DBT** (0.40 g, 2.17 mmol) in dry THF (8 mL) was added *n*-butyllithium (1.2 mL, 1.4 eq). The solution was allowed to warm up to room temperature and stirred for 6 h. The solution was then cooled to –40 °C, and *N*-fluorobenzenesulfonimide (0.69 g, 2 eq) in dry THF (10 mL) was added to the reaction pot. The solution was allowed to warm up to the room temperature and was stirred for another 16 hours. The reaction

mixture was treated with saturated ammonium chloride solution and then washed with water and brine. The organic layer was dried with MgSO4, and solvent was removed using a rotary evaporator to give solid mixture of compounds. The compound was purified by column chromatography (hexane/silica). ^{1}H NMR (300 MHz): δ 8.16-8.13 (m, 1H), 7.93 (dd, 1H, J = 0.6 Hz, 8.1 Hz), 7.91-7.88 (m, 1H), 7.54-7.47 (m, 2H), 7.43 (td, 1H, J = 4.8 Hz, 8.1 Hz), 7.20 (td, J 0.9 Hz, 8.1 Hz). ^{13}C NMR (300 MHz): δ 159.6 (d, J = 79.8 Hz), 139.7 (d, J = 4.2 Hz), 139.1 (d, J = 18.9 Hz), 135.4 (d, J = 9.0 Hz), 127.5, 126.0 (d, J = 27 Hz), 124.9, 123.2, 122.2, 117.4 (d, J = 13.5 Hz), 112.4, 112.

The oxidation of the product to the sulfoxide **6** was done without further purification by the general procedure outlined previously using *m*CPBA. The product was purified using preparatory TLC (1:1 hexane/ethyl acetate). ^{1}H NMR (300 MHz): δ 7.99 (1H, J = 0.6 Hz, 7.5 Hz), 7.80 (dd, 1H, J = 0.6 Hz, 7.2 Hz), 7.64-7.58 (m, 3H), 7.54 (td, 1H, J = 1.2 Hz, 4.5 Hz), 7.19-7.13 (m, 1H). ^{13}C NMR (300 MHz): δ 163.7, 160.3, 145.6, 140.6 (d, J = 13.2 Hz), 136.6 (d, J = 9.6 Hz), 135.6 (d, J = 30.9 Hz), 132.9, 130.4, 127.8, 122.6, 117.9 (d, J = 13.8 Hz), 116.8 (d, J = 79.5 Hz).

4-Bromomethyldibenzothiophene oxide

4-Bromomethyldibenzothiophene was prepared from 4-methyldibenzothiophene using a known procedure of Kudo.[49] The oxidation to the sulfoxide was done without further purification by the general procedure outlined previously using *m*CPBA. ^{1}H NMR (400 MHz): δ 8.01 (d, 1H, J = 7.6 Hz), 7.81 (d, 1H, J = 8.0 Hz), 7.76 (d, 1H, J = 7.6 Hz), 7.62 (td, 1H, J = 1.2 Hz, 7.6 Hz), 7.59 (t, 1H, J = 7.6 Hz), 7.53 (td, 1H, J = 1.2 Hz, 7.6 Hz), 7.48 (d,

1H, J = 7.6 Hz), 4.93 (dd, 2H, J = 10.8 Hz, 218 Hz). ^{13}C NMR (400 MHz): δ 144.7, 143.3, 138.8, 138.1, 136.8, 133.5, 132.8, 131.0, 130.0, 127.7, 122.3, 122.1, 28.0.

4-(methylthio)dibenzothiophene oxide (2a), 4–(methylthiomethyl)dibenzothiophene oxide (2b), 4-(methylthio)dibenzothiophene (7a), and 4-(methylthiomethyl)dibenzothiophene (7b)

4-Fluorodibenzothiophene oxide, 4-bromomethyldibenzothiophene oxide, 4–fluorodibenzothiophene or 4-bromomethyldibenzothiophene, as appropriate, was dissolved in anhydrous DMF (5 mL/1 mg, approximately 50 mg scale). Sodium thiomethoxide (3 eq), dissolved in about 10 mL DMF, was added to the solution and the temperature was raised to 90 °C for one day. The reaction mixture was quenched with sodium bicarbonate and extracted with chloroform. The organic layer was washed with water until neutral (pH paper) and dried over magnesium sulfate. The solvent was removed and the product was purified using preparatory TLC using 1:1 hexane, ethyl acetate mixture as the eluent.

2a: Yield 65%. ^{1}H NMR (300 MHz): δ 8.00 (dq, 1H, J = 0.6 Hz, 7.5 Hz), 7.79 (dq, 1H, J = 0.6 Hz, 7.5 Hz), 7.61 (tt, 2H, J = 1.2 Hz, 7.8 Hz), 7.56 (t, 1H, J = 7.8 Hz), 7.52 (td, 1H, J = 1.2 Hz, 7.5 Hz), 7.36 (dd, 1H, J = 1.2 Hz, 7.8 Hz), 2.65 (s, 3H). ^{13}C NMR (400 MHz): δ 145.1, 143.2, 141.1, 138.2, 137.0, 133.4, 132.6, 130.0, 127.6, 127.5, 122.3, 118.9. MS(EI) *m/z* 246 (M+), 229, 216.

2b: Yield 55%. ^{1}H NMR (300 MHz): δ 7.98 (dq, 1H, J = 0.6 Hz, 7.5 Hz), 7.81 (dq, 1H, J = 0.6 Hz, 7.5 Hz), 7.71 (dd, 1H, J = 1.2 Hz, 7.5 Hz), 7.60 (td, 1H, J = 1.2 Hz, 7.5 Hz),

7.56 (t, 1H, J = 7.5 Hz), 7.51 (td, 1H, J = 1.2 Hz, 7.5 Hz), 7.45 (d, 1H, J = 7.2 Hz), 4.18 (dd, 2H, J = 14.1 Hz, 24.0 Hz), 2.10 (s, 3H). ^{13}C NMR (400 MHz): δ 140.4, 138.9, 136.7, 135.9, 133.4, 128.8, 127.5, 125.4, 125.1, 123.1, 122.2, 122.0, 38.1, 15.6. MS(EI) *m/z* 244 (M-16+), 243, 227, 197. MS (Ion Trap) m/z 261 (M+1+), 244, 227, 197.

7a: Yield 65%. ^{1}H NMR (300 MHz): δ 8.16-8.13 (m, 1H), 8.02 (dd, 1H, J = 1.8 Hz, 6.9 Hz), 7.93-7.89 (m, 1H), 7.50-7.42 (m, 4H), 2.54 (s, 3H). MS(EI) m/z 230 (M+), 215, 184, 171. Data matched reported spectra from alternate preparative route.[50]

7b: Yield 60%. ^{1}H NMR (300 MHz): δ 8.18-8.15 (m, 1H), 8.11 (td, 1H, J = 1.2 Hz, 7.5 Hz), 7.91-7.89 (m, 1H), 7.51-7.43 (m, 3H), 7.40 (dd, 1H, J = 1.2 Hz, 7.5 Hz). ^{13}C NMR (400 MHz): δ 133.5, 130.7, 128.2, 128.0, 127.5, 126.3, 125.3, 124.8, 124.4, 123.0, 121.9, 121.7, 29.9, 12.0. MS(EI) *m/z* 244 (M+), 197, 184. The immediate precursor of **7b** was (4-bromomethyl)dibenzothiophene, which was not completely purified. The reaction mixture of **7b** contained a small quantity of the starting material and 4-methyldibenzothiophene. All three compounds has very similar chromatographic behavior; hence **7b** could not be purified completely. But the proton-NMR spectrum shows **7b** is the major component in the mixture, and GC-MS analysis also demonstrates the major peak is **7b**. Because this was a potential product, rather than a starting material for photochemistry, we did not pursue quantitative purification.

4-methylsulfinyldibenzothiophene (11a)

Compound **11a** was made by the oxidation of **7a** using the same general procedure used for making other **DBTO**s. One equivalent *m*CPBA could only oxidize the aryl-alkyl sulfide leaving the ring sulfur intact. The compound was purified using preparatory TLC (1:1 methylene chloride/ethyl acetate). Yield 70%. ^{1}H NMR (300 MHz): δ 8.43 (dd, 1H, J = 1.2 Hz, 7.8 Hz), 8.24-8.21 (m, 1H), 8.12 (dd, 1H, J = 1.2 Hz, 7.8 Hz), 7.95-7.92 (m, 1H), 7.67 (t, 1H, J = 7.8 Hz), 7.58-7.54 (m, 2H), 3.19 (s, 3H). ^{13}C NMR (300 MHz): δ 140.3, 138.3, 138.0, 134.4, 134.2, 128.2, 127.5, 126.7, 125.3, 125.1, 122.9, 122.1, 43.1. MS(EI) *m/z* 246 (M+), 231, 182.

4-(2-Propylthioethyl)dibenzothiophene oxide (2c) and 4-(3-propylthiopropyl)-dibenzothiophene oxide (2d)

4-Vinyldibenzothiophene oxide (62 mg, 0.27 mmol) or 4-allyl dibenzothiophene oxide (23 mg, 0.096 mmol), AIBN (10 mol%), and propanethiol (3.6 eq) were dissolved in 10 mL CCl_4. The reaction mixture was refluxed under Argon for one day. Then the reaction mixture was washed with 1N sodium hydroxide, followed by several portions of water until the solution became neutral. Then the extract was dried over anhydrous magnesium sulfate. Purification by preparatory TLC (1:1 hexane/ethyl acetate) gave pure **2c** (50 mg, 60%) or **2d** (13 mg, 43%).

2c: ^{1}H NMR (300 MHz): δ 7.98 (d, 1H, J = 7.8 Hz), 7.79 (d, 1H, J = 7.5 Hz), 7.54 (t, 1H, J = 7.8 Hz), 7.50 (td, 1H, J = 1.2 Hz, 7.5 Hz), 7.32 (d, 1H, J = 7.5 Hz), 3.37 (t, 2H, J = 7.5 Hz), 3.09-2.86 (m, 2H), 2.61 (t, 2H, J = 7.5 Hz), 1.66 (sextet, 2H, J = 7.5 Hz), 1.01 (t, 3H,

J = 7.5 Hz). ^{13}C NMR (300 MHz): δ 144.8, 143.6, 142.2, 137.7, 137.5, 133.1, 132.7, 130.7, 129.7, 127.5, 122.1, 120.3, 34.5, 33.9, 33.1, 23.1, 13.7. MS(EI) *m/z* 302 (M+), 285, 251, 243.

2d: ^{1}H NMR (300 MHz): δ 7.98 (dd, 1H, J = 0.6 Hz, 7.2 Hz), 7.80 (dd, 1H, J = 0.6 Hz, 7.5 Hz), 7.67 (dd, 1H, J = 1.2 Hz, 7.5 Hz), 7.60 (dt, 1H, J = 1.2 Hz, 7.5 Hz), 7.53 (t, 1H, J = 7.5 Hz), 7.50 (dt, 1H, J = 1.2 Hz, 7.5 Hz), 7.30 (d, 1H, J = 7.2 Hz), 3.33-3.10 (m, 2H), 2.64 (t, 2H, J = 7.5 Hz), 2.54 (t, 2H, J = 7.5 Hz), 2.19-2.09 (m, 2H), 1.63 (septet, 2H, J = 7.5 Hz), 1.00 (t, 3H, J = 7.5 Hz). ^{13}C NMR (400 MHz): δ 149.5, 145.9, 143.4, 137.5, 135.0, 133.1, 132.6, 130.3, 129.7, 127.6, 122.1, 119.9, 34.3, 32.2, 31.7, 30.9, 23.2, 13.8. MS(EI) *m/z* 316 (M+), 223.

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CHAPTER IV

PHOTOCHEMISTRY OF THIOPHENE-*S*-OXIDE DERIVATIVES

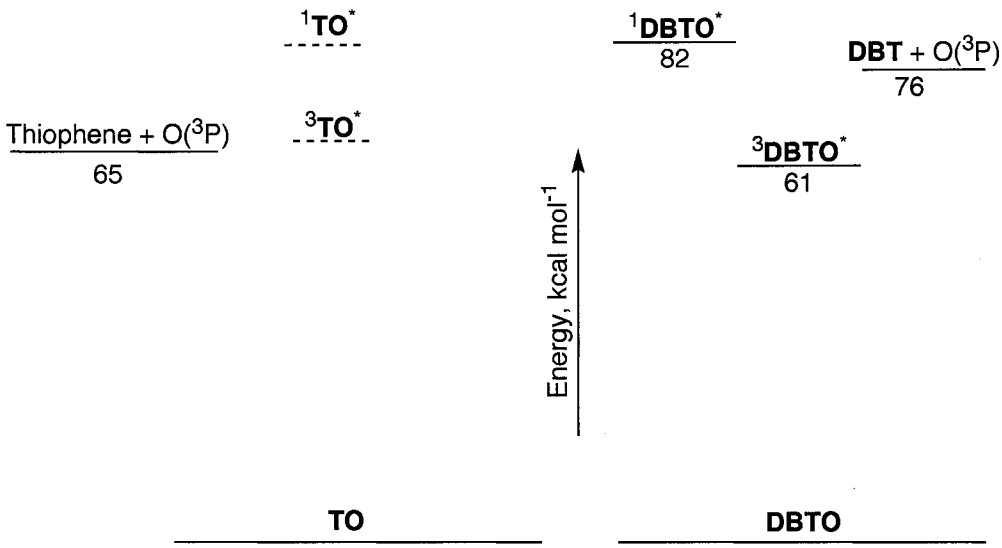
Abstract: Thiophene oxides (**TO**s) with bulky substituents were prepared. Photolysis of 2,5-bis(trimethylsilyl) **TO** in benzene showed a fourteen-fold increase in the quantum yield of deoxygenation compared to **DBTO**. Photolysis of 2,5-di-*tert*-butyl **TO** produced the corresponding furan exclusively. 3,4-Dibenzyl and 3,4-diphenyl **TO**s did not produce any thiophene upon photolysis. The photochemistry of **TO**s is highly substituent dependent but there could be a mechanistic analogy between the deoxygenation of **DBTO** and **TO**.

4.1 Introduction

Photolysis of **DBTO** produces **DBT** and triplet atomic oxygen [$O(^3P)$] as the major products.[1-4] Although there is no direct evidence for the production of $O(^3P)$, all currently available evidence is consistent with its formation.

The fluorescent singlet energy of **DBTO** is about 82 kcal mol^{-1}, and the phosphorescent triplet energy is about 61 kcal/mol,[3,5] whereas the S-O bond dissociation energy has been estimated to be 75-77 kcal/mol using computational methods.[5] From an energetic viewpoint, it is clear that the bond cleavage is not taking place from the emissive triplet surface, although the resulting products are in a net triplet state. Recently it has been shown that heavy atom substitution increases the quantum yield of deoxygenation by a moderate factor when the heavy atoms were attached at the various positions of **DBTO**,[6] and by a large factor when the sulfur atom was substituted by another heavy atom in its group, selenium.[7]

In the case of thiophene-*S*-oxide (**TO)** derivatives, the S-O bond cleavage energy (61-65 kcal/mol) is much lower than that of **DBTO**.[5] At the same time, thiophene oxides will have an excitation energy that is at least somewhat higher than that of **DBTO**. Absorption spectra of **TO** derivatives show λ_{max} at 323-324 nm,[8,9] which is in the same region as **DBTO**. It is also likely that **TO** derivatives will have triplet energies higher than their S-O bond cleavage energies. This could make **TO**s strong substrates for $O(^3P)$ production, provided the deoxygenation mechanism is same as that of **DBTO**.



Scheme 1. Relative energetics for **DBTO** and **TO** excited states and S-O bond cleavage energies.

4.1.1 Detection of the adduct of $O(^3P)$ with acetonitrile

All experimental evidence for the formation of $O(^3P)$ from the photodeoxygenation of **DBTO** is indirect. Detection of the complex between acetonitrile and $O(^3P)$, (CH_3CN^+-O^-), by a laser flash photolysis technique using pyridine-*N*-oxide as the source of $O(^3P)$ was

demonstrated by Bucher and Scaiano.[10] A similar effort was undertaken in our lab to detect the adduct of acetonitrile and O(^{3}P) originating from **DBTO**. Unfortunately, no transient absorption was observed at 325 nm, corresponding to that complex. However, it is likely that the signal would be outside the detection limit of the system due to the low quantum yield of deoxygenation of **DBTO** (0.01 at 266 nm). As mentioned in the previous section, the bond dissociation energy of thiophene oxide was calculated to be 61 kcal/mol. Based on its low bond dissociation energy, **TO** will be a strong candidate for laser flash photolysis experiments.

4.1.2 Synthetic Challenge

Unlike **DBTO**, photochemical studies of **TO** derivatives are not well documented. At least, it is fair to say that there are no definitive mechanistic studies reported for the deoxygenation of **TO**, though a few papers have appeared with interesting results.[11-13] Until recently, there were two main challenges that were responsible for the lack of knowledge about this relatively simple molecule. The first challenge was to synthesize thiophene-*S*-oxide, and the second challenge was to handle it at ambient temperature.

TO has been thought of as an intermediate in the peracid oxidation of thiophene to thiophene-*S*,*S*-dioxide, since it has not been isolated as a product after the completion of the reaction. There are several reasons for **TO** being a non-isolable molecule in those reaction conditions. For most sulfides, the first oxidation is faster than the second, allowing isolation of the sulfoxide. However, in this instance, the rate of oxidation from thiophene oxide to thiophene-*S*,*S*-dioxide is higher than the rate of oxidation from thiophene to thiophene-*S*-oxide. The first step is slower, because thiophene loses a significant amount of aromaticity

to form the sulfoxide. Hence, oxidation of thiophene almost always leads to the thiophene-*S,S*-dioxide derivative.

The second problem arises from the inherent reactivity of **TO** and its derivatives. Even when thiophene-*S*-oxide is formed in low yield it dimerizes via a Diels-Alder reaction (Figure 1).

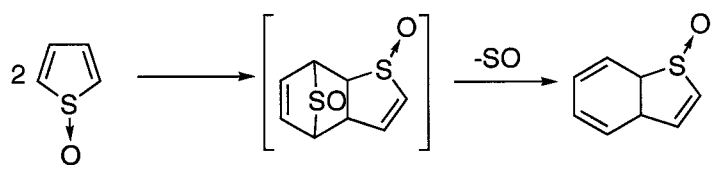


Figure 1. Diels-Alder dimerization of thiophene-*S*-oxide.

The first successful synthesis of a substituted thiophene oxide was reported by Mock in 1970.[8] He used sterically bulky substituted thiophenes as the starting material to prevent the dimerization of the sulfoxide. The oxidation of 2,5-di-*t*-butyl thiophene **1** with one equivalent of *m*CPBA gave approximately 5% yield of the desired sulfoxide **2**, along with sulfone **3** and unreacted starting material (Figure 2).

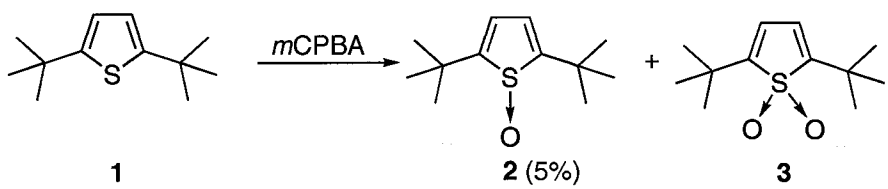


Figure 2. First successful synthesis of a substituted thiophene-*S*-oxide

Mansuy *et al.* reported another successful synthesis of 2,5-diphenyl thiophene oxide **5** in 1995.[14] In their synthesis they used a mixture of trifluoroacetic acid and hydrogen peroxide as the oxidant. The presence of a proton acid (or Lewis acid) could serve a significant role in the oxidation step. It may activate the peracid, or it may complex with the thiophene-*S*-oxide and make the sulfur relatively electron poor so that further oxidation does not take place. Compound **5** was stable at – 20 °C but slowly decomposed over a few days at room temperature to form a secondary product **6**. In this report the authors also provided the first complete structural characterization of a thiophene-*S*-oxide.

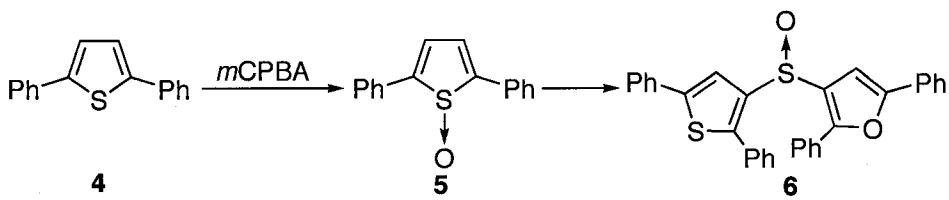


Figure 3. Synthesis of 2,5-diphenyl thiophene-*S*-oxide

Recently more successful syntheses of thiophene-*S*-oxides were reported by using two main pathways, which were free of the complexation problems faced during the reaction shown in Figure 3. The first pathway is the improved direct oxidation of thiophene by using a peracid in the presence of a Lewis acid.[11,13-17] In the second pathway substituted zirconacyclopentadienes are reacted with sulfur dioxide.[18] The first pathway was repeated more often than the second by different research groups, probably because of its versatility and use of relatively common reagents.

Furukawa *et al.* were the first to use an organic peracid with a borontrifluoride/diethyl ether complex as a Lewis acid additive to successfully synthesize 2,5-bis(silyl)thiophene-*S*-

oxides.[16] Nakayama also used the same reagent to successfully synthesize several thiophene -*S*-oxides with sterically bulky groups at the 3,4- or 2,4-positions of thiophene.[19-21] Detailed synthetic schemes will be illustrated later in this chapter.

Fagan and Nugent first proposed an alternate route to prepare thiophene-*S*-oxide, without making a thiophene intermediate.[22,23] The reaction of $Cp_2ZrC_4Ph_4$ with diphenyl acetylene **7** produced **8**, which reacted with thionyl chloride to give tetraphenylthiophene-*S*-oxide **9** in moderate yield. This method, however, was limited to tetraphenylthiophene-*S*-oxide synthesis. Jiang and Tilley further improved the method by modifying the reagents.[18] This procedure was more versatile and gave a better yield of thiophene-*S*-oxide than Fagan and Nugent's procedure described above. One example of this reaction is shown in Figure 4, where the substituted thiophene-*S*-oxide **11** was prepared. This reaction was proposed to proceed via an intermediate analogous to structure **8**, as shown in the first reaction.

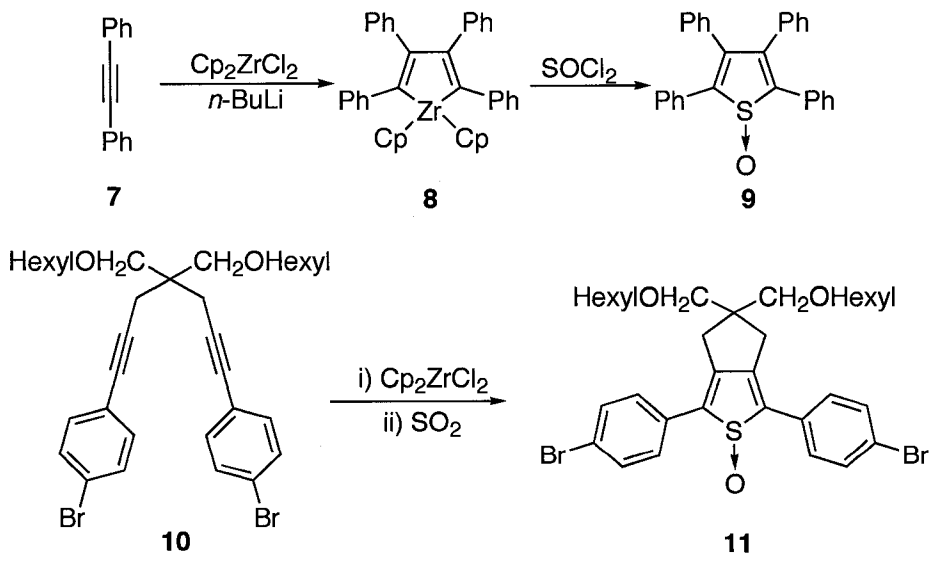


Figure 4. Synthesis of thiophene-*S*-oxides via zirconacyclopentadiene complex

4.1.3 Structure of thiophene oxide

There are two possible structures for thiophene-*S*-oxide (Figure 5). Ordinary sulfoxides are pyramidal with a sp^3 hybridized sulfur, similar to structure **B**. Thiophene is an aromatic compound; for thiophene-*S*-oxide to also be an aromatic compound it must be planar like structure **A**. The effect of structure on aromaticity and vice versa will be discussed later.

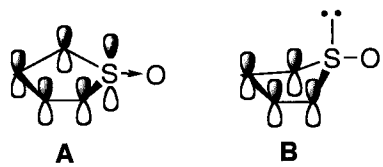
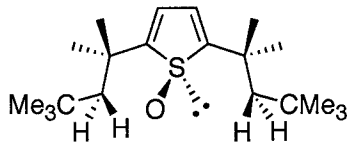


Figure 5. Two possible structures for thiophene-*S*-oxide

Mock was the first to synthesize and investigate the structure of substituted thiophene-*S*-oxides. He showed that Diels-Alder dimerization can be slowed down by putting bulky groups at the 2- and 5- positions of the thiophene ring and he was able to investigate the structures of several substituted thiophene sulfoxides using UV-vis and NMR techniques.[8] He synthesized substituted thiophene oxide **12** and studied the pyramidal inversion process by proton NMR. At -10 °C the NMR data showed that the side chain protons of **12** were non-equivalent (two doublet of doublets peaks). This anisotropy was probably coming from the sulfoxide group, since there was no such anisotropy observed for the corresponding sulfide or sulfone compounds.



12

Figure 6. Stereochemical representation of 2,5-di-*tert*-octylthiophene-*S*-oxide

When the temperature was raised the quartets started to broaden, and above 60 °C they coalesced into a singlet. The free energy of activation derived from the rate constant data at coalescence temperature was about 14.8 kcal/mol. From these data it was concluded that the thiophene oxide was a non-planar compound similar to structure **B** shown in Figure 5, and it underwent pyramidal inversion through a planar transition state or intermediate which is denoted by structure **A** in Figure 5. This conclusion was supported by Mansuy *et al.* who used an X-ray diffraction technique to establish the structure of 2,5-diphenylthiophene-*S*-oxide.[14] Computational work by Jenks *et al.* at the RHF level showed that the sulfur atom is slightly below the plane defined by the other atoms in the ring, and the oxygen atom is substantially above the plane.[5] Recently Bongini and coworkers computed the structure of thiophene-*S*-oxide using MP2/6-31G(d) *ab initio* calculation and indicated a similar non-planar structure with the sulfur atom lying outside the plane formed by the other four atoms by 0.26 Å.[9] Using the same level of theory they also calculated the barrier of inversion for the sulfoxide to be 13.5 kcal/mol, which was in agreement with Mock's experimental value.[8] The inversion barrier for non aromatic sulfoxides reported by Mislow *et al.* was around 37-42 kcal/mol.[24] Jenks *et al.* also calculated the inversion barrier to be approximately 25 kcal/mol lower than that of DMSO, which was also comparable to the experimental values.[5]

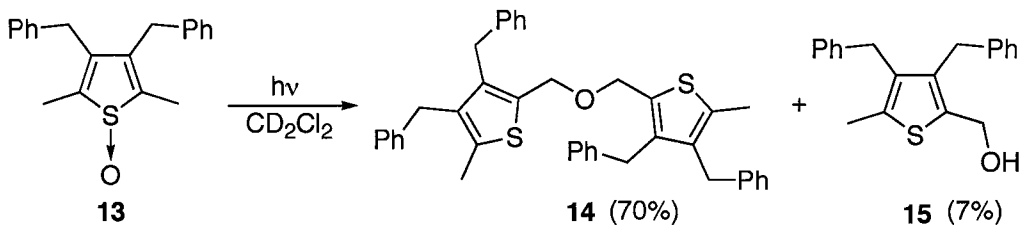
This lower barrier of inversion experienced by thiophene-*S*-oxide is due to the aromatic stabilization of the planar transition state that is not present in the equilibrium structure.

4.1.4 Characteristics of excited state thiophene oxides

The electronic spectra of thiophene oxides show two absorption maxima: one near 250 nm and the other one near 320 nm. The higher wavelength maximum is not present in the corresponding thiophene compounds. Mock reported a blue shift of the absorption maxima in polar solvents,[8] which indicates that the excited singlet state of the thiophene-*S*-oxide is $n\pi^*$ in nature, or at least that it is less polar than the ground state. However, recent theoretical calculations by Bongini *et al.* by 4 × 4 singly excited CI ZINDO/S/PM3 analysis show that the low wavelength absorption in thiophene-*S*-oxide is due to the mixing of transitions involving both S-O and π orbitals, whereas, the high wavelength absorption is due to the HOMO-LUMO π-π^* transition.[9] It was also mentioned that the lone pairs of oxygen were not involved in the HOMO-LUMO transition.

4.1.5 Photochemistry of thiophene-*S*-oxides

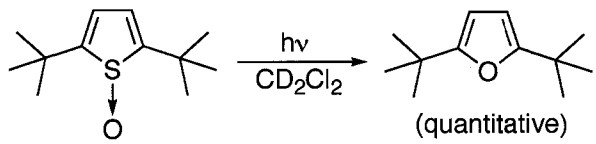
Before this work, the photochemistry of thiophene-*S*-oxides was investigated mainly by Thiemann's group.[13,25] Photolysis of 3,4-dibenzyl-2,5-dimethylthiophene-*S*-oxide **13** in dichloromethane with a high-pressure mercury lamp produced a mixture of **14** and **15** in 70% and 7% yield respectively (Figure 7).



13 **14** (70%) **15** (7%)

Figure 7. Photolysis of 3,4-dibenzyl-2,5-dimethylthiophene-*S*-oxide

On the other hand, previous experimental results in Jenks' laboratory showed that the photolysis of 2,5-di-*t*-butylthiophene-*S*-oxide **2** produced the corresponding furan **17**.[26] This reaction was also observed by Thiemann *et al.*[13] Jenks *et al.* also reported that the photolysis of tetraphenylthiophene-*S*-oxide produced the corresponding thiophene as the main product and the corresponding furan as the minor product.[26]



2 **17**

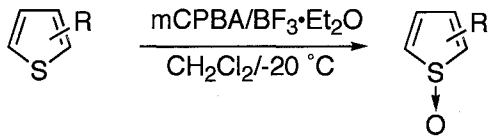
Figure 8. Photolysis of 2,5-di-*t*-butylthiophene-*S*-oxide

4.2 Results

Compounds of interest

Thiophene oxides with bulky substituents at the 3,4- or 2,5- or 2,4-positions were shown to be stable in ambient conditions.[20] We proposed to synthesize sulfoxides **2** and **22-24** using literature methods from their immediate sulfide precursor **1**, **18** and **19-21** (Scheme 2).[16,19,20,27,28] Four sulfoxides **2**, **22** and **23c-d** were prepared successfully from the

corresponding thiophenes in moderate yield (20-25%). Compound **20-21** can be synthesized from **19a-b** by isomerization. Syntheses of other thiophenes will be discussed in detail.



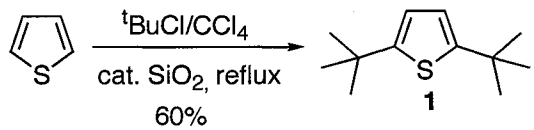
R = 2,5-di-*tert*-butyl, **1**
R = 2,5-bis(trimethylsilyl), **18**
R = 3,4-di-*tert*-butyl, **19a**
R = 3,4-di-neopentyl, **19b**
R = 3,4-diphenyl, **19c**
R = 3,4-dibenzyl, **19d**
R = 2,4-di-*tert*-butyl, **20**
R = 2,4-dineopentyl, **21**

R = 2,5-di-*tert*-butyl, **2**
R = 2,5-bis(trimethylsilyl), **22**
R = 3,4-di-*tert*-butyl, **23a**
R = 3,4-di-neopentyl, **23b**
R = 3,4-diphenyl, **23c**
R = 3,4-dibenzyl, **23d**
R = 2,4-di-*tert*-butyl, **24a**
R = 2,4-dineopentyl, **24b**

Scheme 2. Preparation of substituted thiophene oxides

Synthesis of 2,5-di-*tert*-butyl thiophene 1

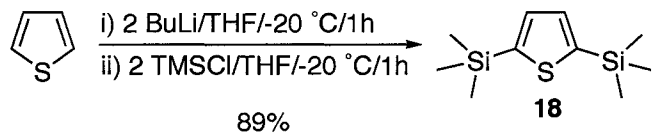
2,5-Di-*t*-butyl thiophene was prepared by treatment of thiophene with *tert*-butyl bromide in refluxing carbon tetrachloride with a silica gel catalyst following a literature method (Scheme 3).[29]



Scheme 3. Preparation of 2,5-di-*tert*-butyl thiophene

Synthesis of 2,5-bis(trimethylsilyl)thiophene 18

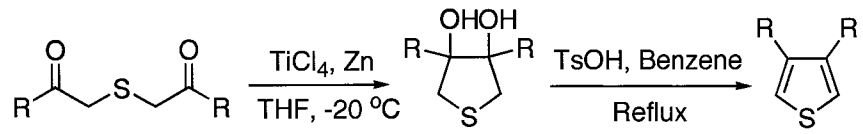
Compound **18** was prepared using a literature method.[30] Lithiation of thiophene using two equivalents of butyllithium and subsequent treatment with two equivalent of trimethylsilyl chloride produced **18** in 90% yield (Scheme 4).



Scheme 4. Preparation of **18**

Preparation of 3,4-disubstituted thiophenes 19a-d

Substituted thiophenes **19a-d** were synthesized from the titanium chloride-zinc catalyzed ring-closure reaction of sulfanyl diketones **25a-d** followed by dehydration, using a literature method (Scheme 5).[17,27] The key step in this reaction is the McMurry coupling. The yield of the diol intermediate **26a-d** varied depending upon the substituent R. For diphenyl compound **25c**, the reaction was reliable and reproducible (75% yield); for di-*tert*-butyl **25a** the reaction was less reliable (50% yield maximum). However, for dineopentyl and dibenzyl, the reaction produced very little or no **26b** or **26d**. Although this is unfortunate, the unreliability of the McMurry reaction is not unprecedented in the scientific community.[31]



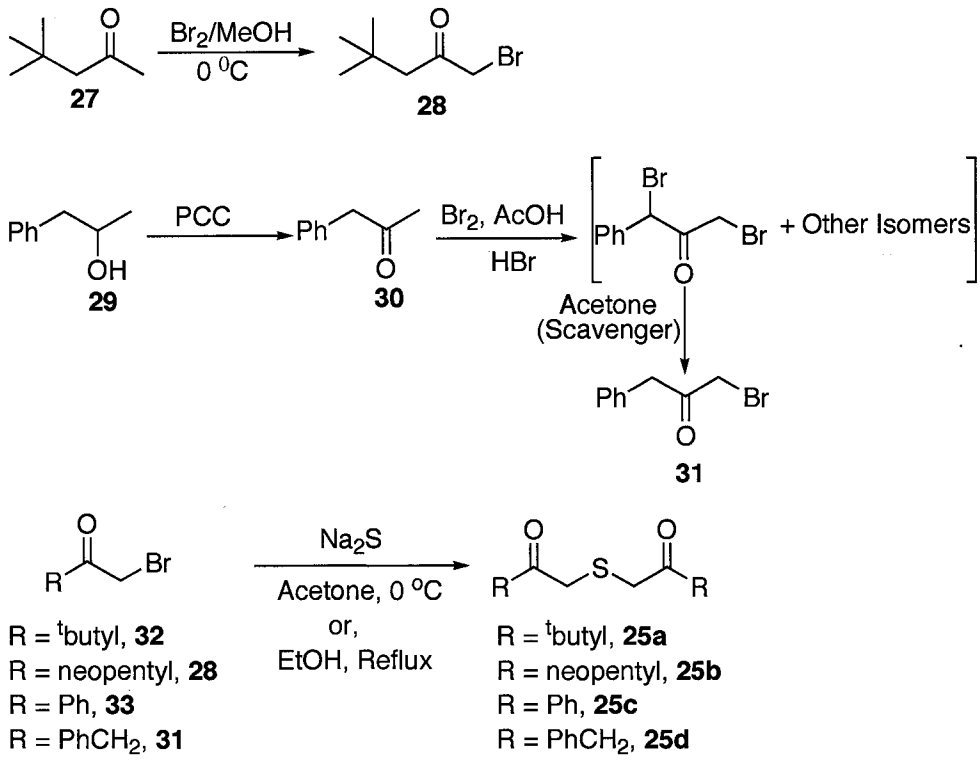
R = ^{t}butyl, **25a**
R = neopentyl, **25b**
R = Ph, **25c**
R = $PhCH_2$, **25d**

R = ^{t}butyl, **26a**
R = neopentyl, **26b**
R = Ph, **26c**
R = $PhCH_2$, **26d**

R = ^{t}butyl, **19a**
R = neopentyl, **19b**
R = Ph, **19c**
R = $PhCH_2$, **19d**

Scheme 5. General scheme for making 3,4-disubstituted thiophenes

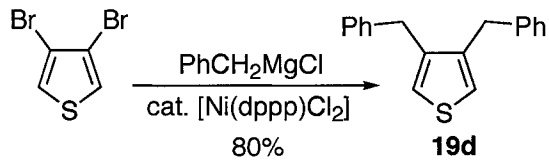
Sulfanyl diketones were easily synthesized[32] by treating sodium sulfide either with commercially available haloketones **32** and **33** or from **28** and **31**, which were prepared by halogenations of the corresponding ketones **27** and **30** (Scheme 6). Neopentyl methyl ketone **27** was commercially available and was selectively brominated to **28** in 60% yield using a literature method.[19] Phenyl acetone **30** was prepared from 2-phenylpropan-2-ol **29** by PCC oxidation quantitatively. In the next step non-selective bromination of phenyl acetone **30** using excess bromine, followed by selective debromination using acetone as a scavenger, gave 1-bromo-3-phenylpropanone **31** in 60% yield.[33]



Scheme 6. Preparation of Diketosulfides

Alternate method for the preparation of 19d

Although the above-mentioned scheme produced 3,4-dibenzylthiophene **19d**, it was too long and produced our desired product in a low yield. A new method was employed where Ni(II) catalyzed Grignard cross coupling of benzylmagnesium bromide to 3,4-dibromo thiophene yielded our desired product in 80% yield (Scheme 7).[34] This procedure was also applied to make other di-substituted thiophenes like **19a-b**, but none of those produced products in reasonable yields.



Scheme 7. Preparation of **19d** using Grignard cross coupling

Photolysis

Thus far, we have successfully synthesized four different thiophene oxides. They are: 2,5-di-*tert*-butylthiophene-*S*-oxide **2**, 2,5-bis(trimethylsilyl)thiophene S-oxide **22**, 3,4-diphenylthiophene-*S*-oxide **23c**, and 3,4-dibenzylthiophene-*S*-oxide **23d**. Sulfoxide **2** was photolyzed in the past by our group and Thiemann's group.[13,26]

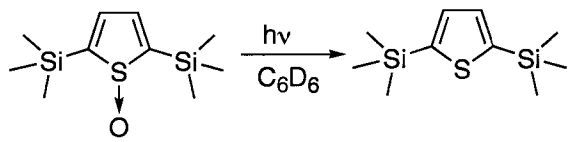
Photolysis of sulfoxide 2

Photolysis of sulfoxide **2** was done in Ar-flushed solvents using a Xe arc lamp coupled to a monochromator set to 320 nm (± 12 nm linear dispersion), which is near the first absorption maximum of **2**. The initial concentration was approximately 5 mM. The photolysis products were analyzed by GC. Photolysis in acetonitrile and benzene shows formation of 2,5-di-*t*-butylfuran as the only product (Figure 8). This result was similar to the one previously reported.[13,26]

Photolysis of sulfoxide 22

Sulfoxide **22** was not stable to the GC conditions, so an alternative analytical technique was required. The reaction was monitored by proton NMR. The sulfoxide was dissolved in $CDCl_3$ and *d6*–benzene in two different experiments. Dioxane was used as an

internal standard in both cases. The NMR tube was irradiated in the Rayonet minireactor with a broad wavelength of light centered at 300 nm. The photolysis shows formation of the corresponding thiophene **18**. No furan was detected in the reaction mixture. The quantum yield of decomposition was calculated to be 0.0092 in $CDCl_3$ and 0.046 in benzene.



22 **18**

Scheme 8. Photolysis of sulfoxide **22**

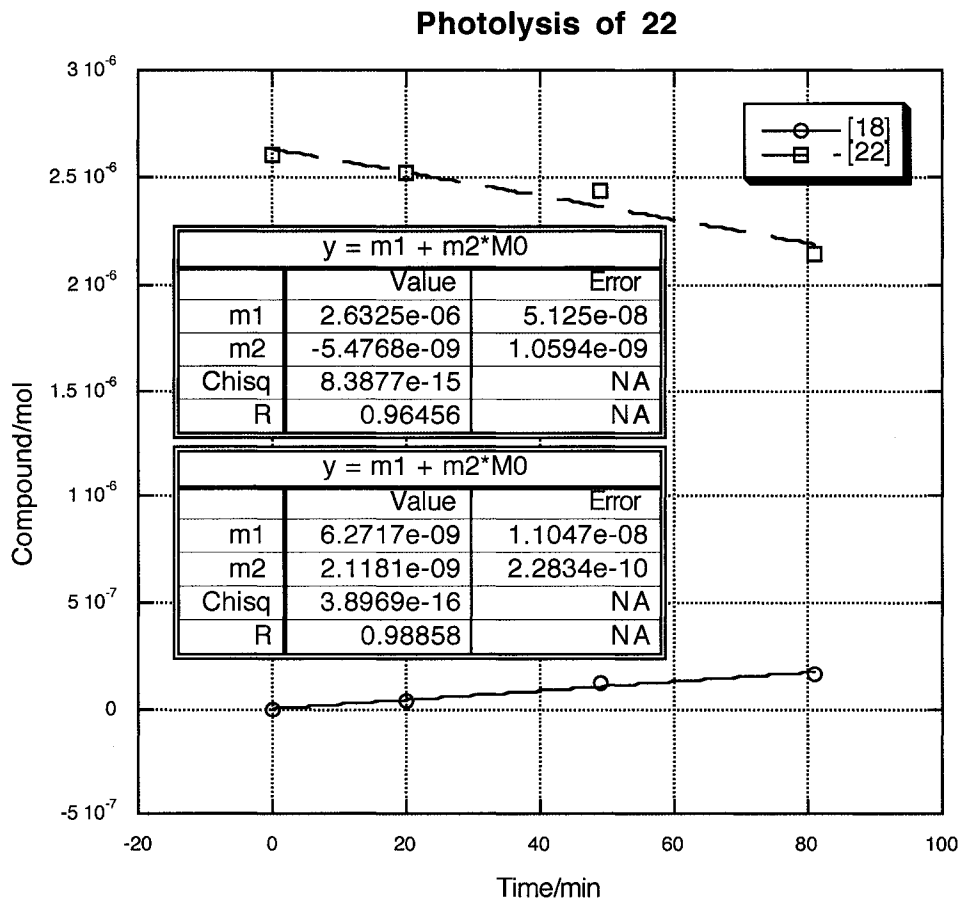


Figure 9. Photolysis of **22** in $CDCl_3$ at 300 nm

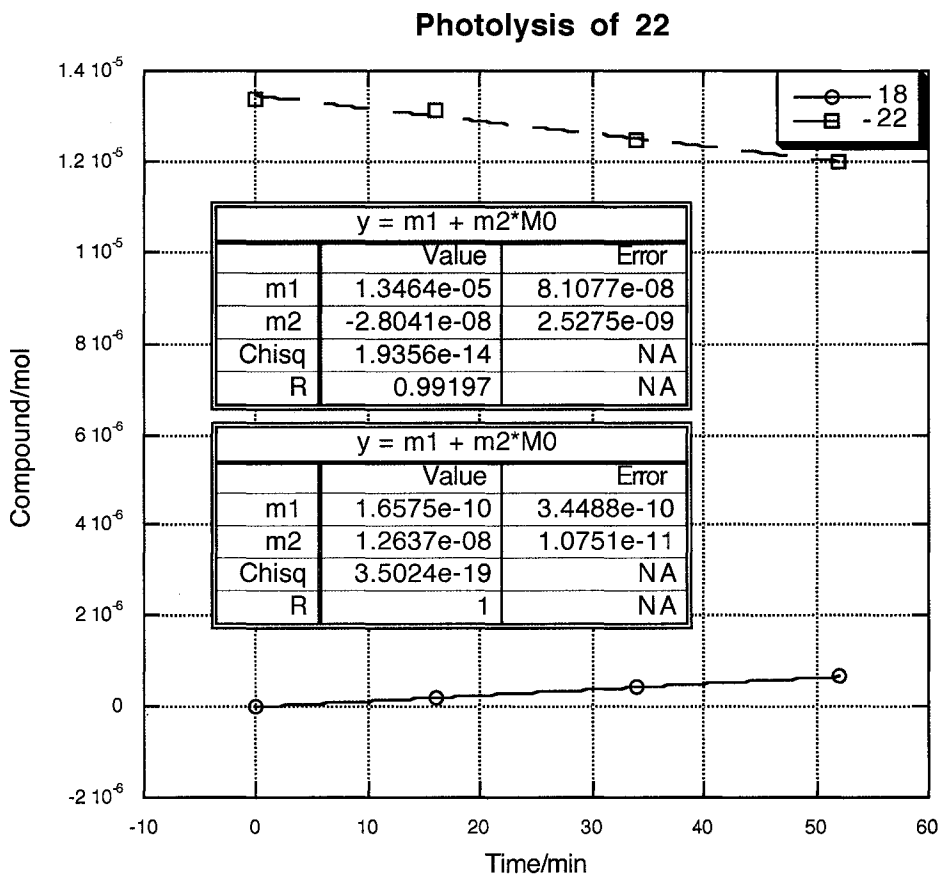
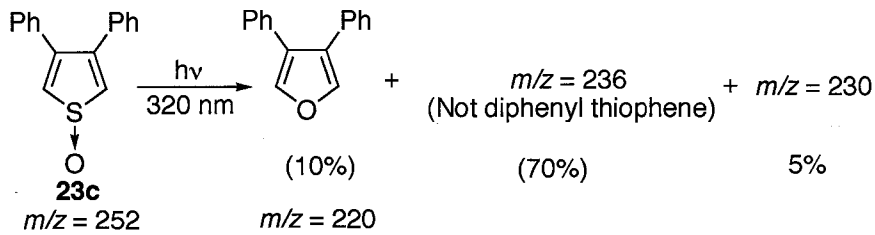


Figure 10. Photolysis of **22** in d_6-benzene at 300 nm

Figures 9 and 10 show the rate of decay of sulfoxide **22** and the growth of sulfide **18**. The points that are plotted in the graph, were obtained by the relative integrations in the NMR runs compared to dioxane. The quantum yield was calculated by using valerophenone as an actinometer,[35] where 1 mL solution of 50 mM valerophenone in benzene was photolyzed using dodecane as an internal standard. Although the photolysis was done in an NMR tube, GC was used to monitor the reaction.

Photolysis of sulfoxide 23c

3,4-Diphenylthiophene S-oxide **23c** was photolyzed under the same condition described for the photolysis of sulfoxide **2**. Upon irradiation this sulfoxide produces a complex reaction mixture. The reaction was monitored by GC and GC-MS. Among the products there were the corresponding furan (10%), and an isomer of diphenylthiophene (70%) but no parent thiophene compound was detected (Scheme 9).



Scheme 9. Photolysis of 3,4-diphenyl thiophene-*S*-oxide

Photolysis of sulfoxide 23d

3,4-Dibenzyl thiophene S-oxide **23d** was synthesized by the general oxidation method, but it is not stable at the elevated temperature used in GC. Naturally, this compound was not detectable in GC. Photolysis was done in acetonitrile but HPLC analysis failed to show formation of the corresponding thiophene. In another experiment the compound was photolyzed in an NMR tube in benzene-d_6 using the same method described above for compound **22**. NMR analysis also did not show the formation of the corresponding analogue. However, it was shown that **23d** decomposes very quickly to produce unknown

products. The quantum yield for the decomposition was very high (1.571). The plot for the decomposition is shown in Figure 11.

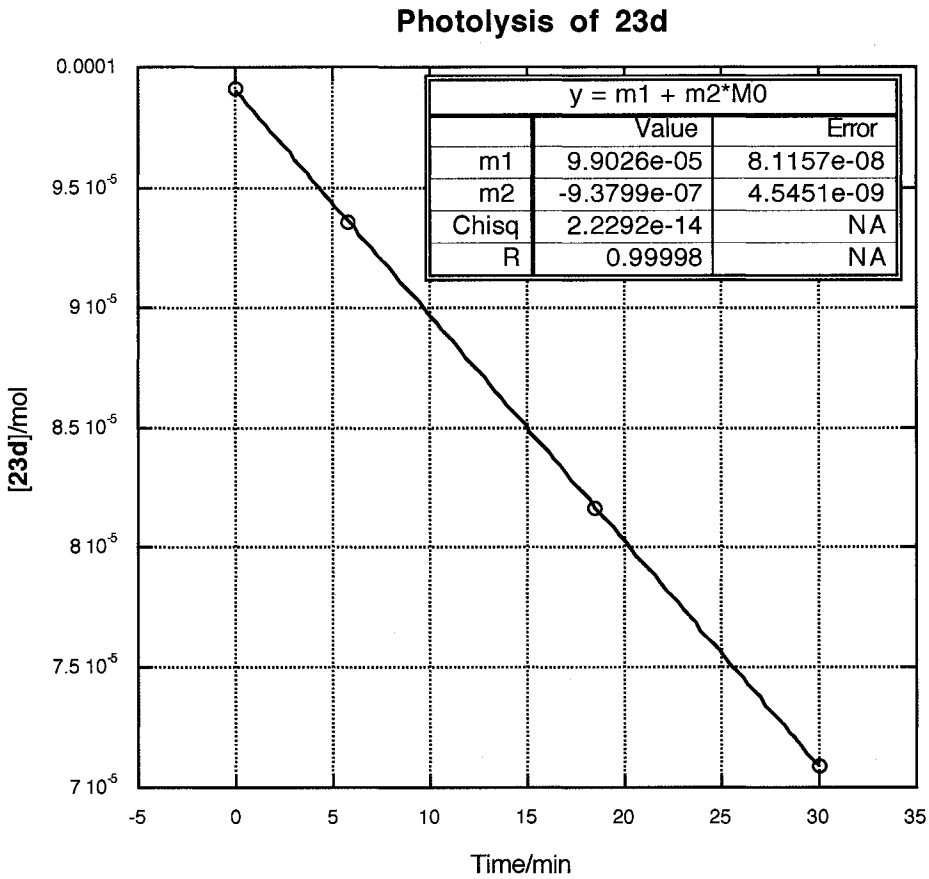
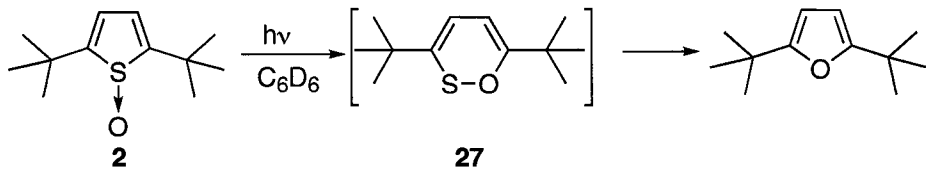


Figure 11. Decomposition of **23d** at 300 nm

4.3 Discussion

Photolysis of **2** produced the corresponding furan as the only product. Even though we are trying to investigate the deoxygenation mechanism of thiophene-*S*-oxides, it is worthwhile to know how the desulfurization process takes place. The proposed mechanism,

which was also presented by Thiemann *et al.*,[25] involves a six-membered ring intermediate shown in scheme 10. The S-S analogue of this intermediate, 1,2-dithiin and its O-O analogue, 1,2-dioxin are known compounds[36,37] but the intermediate **27** itself is not known and is presumably less stable.[37]



2 **27**

Scheme 10. Proposed desulfurization mechanism for thiophene-*S*-oxide **2**

Among other sulfoxides, only sulfoxide **22** produced the corresponding thiophene **18** exclusively. The early results are promising and the deoxygenation quantum yield was calculated to be around 0.0092, which is more than 3 times higher than that of dibenzothiophene oxide. But only about one third of the disappearance was accounted for by the appearance of the thiophene. However, in benzene the efficiency of deoxygenation dramatically increased to 0.0460 but again in this case the appearance of thiophene was almost half of the disappearance. It is possible in the first case that initial concentration of the sulfoxide **22** was low, and it did not absorb all the light but it is also possible that benzene and chloroform have very different effects on the photolysis. The photolysis was done at a low concentration of the starting material (ca. 1-4 mM), and was stopped before 10% conversion of the starting material to avoid any secondary photolysis and to make sure the sulfoxide was absorbing all the light. We wish to use other feasible analytical technique like LC and LC-MS to monitor the reaction. Sulfide **18** has been shown to undergo

decomposition and other reactions at low wavelength irradiation but it does not absorb any light > 300 nm, so the possibility of secondary photolysis was minimized.

Photolysis of sulfoxide **23c** failed to produce any sulfide **19c**, although it produces the corresponding furan as one of the products. The major product in this photoreaction was an unknown compound with the same mass as the sulfide **19c**. At this point it is unknown whether **19c** is isomerizing to the unknown product by a secondary photolysis or if the unknown product is directly coming from the sulfoxide via a non-deoxygenative pathway.

2,5-Dibenzylthiophene-*S*-oxide **23d** was photolyzed in acetonitrile. Monitoring the reaction was difficult since no suitable analytical method was found to detect all the products of the reaction mixture. However, HPLC analysis shows the decomposition of the starting material **23d** in a linear, first order kinetic pathway. Another photolysis was done using NMR as a detection tool for the photoproduct, which also did not indicate formation of any corresponding thiophene. However, the quantum yield of decomposition was calculated to be 1.571, which indicates there is more than one simple pathway for the decomposition. The sulfoxide could be decomposed by a thermal reaction, for which we need to do a control experiment to check whether any thermal reaction is taking place within the time limit of the photoreaction or there could be some kind of chain reaction involved, which is initiated by the irradiation.

Syntheses of some of the compounds were problematic, especially the cyclization by McMurry type coupling was the most difficult step. The reaction worked for compound **26c** really well, worked to some extent but was not reproducible for some compound **26a**, and did not work at all for **26b**. Several techniques, including elevation of temperature and changing solvents was not fruitful. However, other modifications such as using a different catalyst and

solvent combination, or other techniques such as the one shown in scheme 4 will be undertaken to overcome this hurdle.

4.4 Summary

The photolysis results of sulfoxide **22** is promising, although it is too early to draw any conclusions from it. The quantum yield of decomposition in benzene is 0.042, which is considerably higher than **DBTO** but the only about half of the decomposition is accounted for by the formation of thiophene. Also, in chloroform the quantum yield is really low compared to that in benzene. It could be due to the low initial concentration of sulfoxide used in the photolysis in chloroform. Sulfoxide **1** produced the corresponding furan, which is similar to the results already published. The other sulfoxides that were successfully synthesized gave complex product mixtures. Sulfoxide **23c** produced the corresponding furan as a minor product along with other unknown products. The major unknown product had the same mass as the corresponding thiophene **19c**. It is possible that sulfoxide **23c** deoxygenates under the photolysis conditions and that product **19c** undergoes isomerization but direct conversion from the sulfoxide to the unknown product also cannot be ruled out. A control reaction and a full characterization of the product mixture will be undertaken to shed more light on this mechanism. For sulfoxide **23d** the problem is analytical. A suitable method will be applied to monitor the reaction. Proton NMR could be a useful, albeit less sensitive, technique to monitor the photoreaction.

4.5 Experimental Section

General

Reagents and solvents were used without further purification, except as noted. Thiophene was distilled using a short path distillation apparatus. For cyclization of sulfanyl diketones by McMurry type coupling reactions, the glassware and needles were flame dried and the zinc was washed with dilute hydrochloric acid and flame dried under argon prior to use. THF and DME were distilled over sodium and under argon prior to their use in cyclization reactions. Routine gas chromatography and quantification was performed on an instrument with a flame ionization detector. GC-MS analyses were done with either an EI/CI-quadruple MS or a benchtop instrument with an ion trap. All analyses were done using a 30 m 5% phenyl column. All NMR spectra were taken in $CDCl_3$ or d_6-benzene. Most of the compounds synthesized here are known in the literature and already fully characterized, unless otherwise noted. Only proton NMR spectra are given for the known compounds. No further spectral details are mentioned when the proton NMR matched with those already reported.

Photolyses

Photolyses were done in spectro grade solvents, as indicated with initial concentrations in the range of 1 – 5 mM. d_6-Benzene was dried over activated molecular sieves for at least a day before using as a solvent. Dodecane was used as an internal standard for all the photoreactions that were monitored by GC. Dioxane was used as an internal standard when the photoreactions were monitored by proton NMR. Valerophenone was used as an actinometer for quantum yield measurements.[35] Irradiations were carried out with a 75

W Xe arc lamp from PTI, coupled to a matching monochromator or with a fan cooled Rayonet mini-reactor at room temperature using broadly emitting 300 nm fluorescent tubes supplied by Southern New England Ultraviolet. All settings of the monochromator or Rayonet were kept constant during the measurements. Actinometry was repeated frequently to avoid any effect on quantum yield measurement due to any drift of the light flux.

2,5-Di-*tert*-butylthiophene (1)

2,5-Di-*tert*-butylthiophene was prepared by the method of Kamitori.[29] To a mixture of thiophene (2 g, 25 mmol), activated silica gel (6 g) and sodium carbonate (7.6 g, 12 mmol) in carbon tetrachloride (25 mL) was added *tert*-butyl bromide (10.3 g, 75 mmol). The reaction mixture was refluxed for 2 days. Then the mixture was filtered through a fritted funnel. The filtrate was distilled under vacuum using Kugelrohr to give a colorless liquid. Yield: 60%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.63 (s, 2H), 1.39 (s, 18H).

2,5-Bis(trimethylsilyl)thiophene (18)[30]

Thiophene (2 g, 23.8 mmol) was dissolved in anhydrous THF (20 mL) and the solution was cooled down to –20 °C. Butyllithium (23.8 mL, 2.5 M, 59 mmol) was added to the chilled solution dropwise. The resulting solution was warmed up to room temperature and stirred for an hour. Then the solution was again cooled down to –20 °C and trimethylsilyl chloride (9.7 g, 89 mmol) was added to the reaction flask. The resulting solution was warmed to room temperature and stirred for overnight. The solution was concentrated until most of the organic solvent was gone. The mixture was then diluted with ether (100 mL) and washed with dilute hydrochloric acid, dilute sodium bicarbonate, water,

and brine. The organic layer was dried over magnesium sulfate and evaporated to give a light yellow liquid (4.86 g). The proton NMR shows the presence of a pure product so no further purification was necessary. Yield: 89%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34 (s, 2H), 0.33 (s, 18H).

Preparation of 1-bromo-4,4-dimethylpentanone (27)

Bromine (2.8 g, 18 mmol) was added in a single stream to an ice-cold mixture of methyl neopentyl ketone (2 g, 18 mmol) in 5 mL of methanol. The mixture was diluted with 13 mL of water and extracted with ether (4 × 15 mL). The extracts were washed with aqueous sodium bicarbonate and water, dried over magnesium sulfate, and evaporated to give 2.5 g of the 1-bromo-4,4-dimethylpentanone (**27**). This compound was practically pure, so it was used as a starting material without further purification. Yield: 60%. The NMR matched those reported in the literature.[33]

Synthesis of sulfanyl diketones

General procedure: To a stirred refluxing mixture of haloketone (1 eq.) in ethanol, or to an ice-cold mixture of haloketone in acetone, was added a solution of sodium sulfide nanohydrate (0.5 eq.) in water drop by drop over a period of 20 - 30 min (depending upon the amount). Usually the product crystallized from the solution within two hours. When the crystal was not formed the reaction mixture was extracted with toluene, washed with water, dried and evaporated. The product was recrystallized from pentane. In the case of 1-(4,4-dimethyl-2-oxopentylsulfanyl)-4,4-dimethyl-2-pentanone (**25b**) the product produced yellow

oil, which was distilled using a Kugelrohr apparatus. The proton NMR spectra of these synthesized compounds matched those reported in the literature.[32]

1-(3,3-Dimethyl-2-oxo-butylsulfanyl)-3,3-dimethyl-butan-2-one (25a)

Yield: 95%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.53 (s, 2H), 1.18 (s, 9H).

1-(4,4-Dimethyl-2-oxo-pentylsulfanyl)-4,4-dimethyl-pentan-2-one (25b)

Yield: 78%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.27 (s, 4H), 2.45 (s, 4H), 1.03 (s, 18H).

2-(2-Oxo-2-phenyl-ethylsulfanyl)-1-phenyl-ethanone (25c)

Yield: 85%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.98 (m, 2H), 7.60 (dt, 1H), 7.49 (m, 2H), 4.00 (s, 2H).

1-Bromo-3-phenyl-2-propanone (31)

1-Bromo-3-phenyl-2-propanone was prepared using the method of Choi.[33] To a mixture of phenyl acetone (2.0 g, 15 mmol) in acetic acid (5 mL) and 40% hydrobromic acid (2.5 mL) was added bromine (5.2 g, 1.7 mL, 33 mmol) dissolved in acetic acid (7.5 mL) and the reaction mixture was stirred for a day. Then the reaction mixture was concentrated, extracted with methylene chloride, and dried over magnesium sulfate. The solution was concentrated under vacuum for 10 hours to remove bromoacetone produced in the reaction. The residue was passed through a short silica column, and then the compound was purified using flash chromatography (5% EtOAc/95%Hexane) to give pure product. Yield: 60%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40-7.31 (m, 3H), 7.25 (dd,2H), 3.96 (s, 2H), 3.92 (s, 2H).

Synthesis of 3,4-disubstituted tetrahydrothiophene-3,4-diol (26a, 26c)

General procedure: Titanium tetrachloride (3 eq.) was added dropwise over a period of 2-3 hour to a stirred mixture of sulfanyl diketones (1 eq.) and zinc powder (6 eq.) in anhydrous THF at –20 °C for 5 hours. The reaction mixture was quenched by crushed ice. Then the pH of the mixture was adjusted to about 9 by adding saturated sodium carbonate solution. After adding hexane, the whole mixture was stirred for one hour and filtered through a celite pad. The celite and solid material on the filter was washed with additional hexane. The organic layer was washed with water, dried, and evaporated. The products were recrystallized from pentane. The proton NMR spectra matched those reported in the literature.[27]

3,4-diphenyl-tetrahydrothiophene-3,4-diol (26c). Yield: 75%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.21-7.09 (m, 10H), 3.64 (d, 2H, J = 11.7 Hz), 3.45 (s, 2H), 3.18 (d, 2H, J = 12.0 Hz). ^{13}C NMR ($CDCl_3$): δ 139.75, 127.93, 127.64, 126.48, 86.15, 40.29.

3,4-di-*tert*-butyl-tetrahydrothiophene-3,4-diol (26a). Yield: 50%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.33 (s, 2H), 3.29 (d, 2H), 2.81 (d, 2H), 1.25 (s, 18H)

Synthesis of 3,4-disubstituted thiophene from the diols

General procedure: 3,4-diol compound (1 eq) and TsOH (0.13 eq.) in benzene were refluxed for 1 hour. After the reaction, the mixture was washed with saturated sodium

carbonate solution, dried in magnesium sulfate, and evaporated. The crude mixture was purified using column chromatography.

3,4-Diphenylthiophene (19c)[27]

Yield: 80%. ^{1}H NMR ($CDCl_3$): δ 7.361 (s, 2H), 7.30 (m, 6H), 7.24 (m, 4H).

3,4-Dibenzylthiophene (19d)

3,4-Dibenzylthiophene was prepared using a literature method.[34] To a mixture of 3,4-dibromothiophene (1 g, 4.1 mol) and a catalytic amount of dichloro-(diphenylpropylphosphine)-nickel (II) (0.06 g, 2.7 mol%) in dry ether (10 mL) was added dropwise benzylmagnesiumchloride (2M solution in ether, 5 mL, 10 mmol) at 0 °C. Then the reaction mixture was refluxed for a day under argon. The reaction was cooled using an ice-bath and was slowly quenched with 2N hydrochloric acid. Then the organic layer was washed with a 10% sodium hydroxide solution, water, and brine, dried over magnesium sulfate, and evaporated under vacuum. The solid was recrystallized from pentane to give the product in 80% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.30 (m, 4H), 7.22 (m, 2H), 7.15 (m, 2H), 6.84 (s, 2H), 3.83 (s, 4H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 140.5, 140.0, 129.0, 128.6, 126.3, 123.0, 35.5.

Disubstituted thiophene S-oxides

General Procedure: 3,4-Disubstituted thiophenes **1**, **18** and **23c-d** (1 equivalent) were dissolved in dry dichloromethane, typically 40 mL/g starting material. Boron trifluoride-diethyl etherate (3 eq.) was added to this solution and the solution was stirred at –

20 °C for 10 minutes. Then, *m*CPBA (1 eq.) in dry dichloromethane, typically 20 mL per g, was added to the stirred solution dropwise. The solution was stirred at –20 °C under argon for another 2 hours. The mixture was then warmed to room temperature over a few minutes and quenched by addition of aqueous bicarbonate. The aqueous layer was extracted thrice with chloroform and the organic layer was washed with water and brine. Then the solution was dried over magnesium sulfate and concentrated under vacuum. The proton NMR matched those reported in the literature.[11,16,20,27]

2,5-Di-*tert*-butyl thiophene S-oxide (2).[11] Yield: 30%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.20 (s, 2H), 1.39 (s, 18H).

2,5-Bis(trimethylsilyl)thiophene S-oxide (22).[16] Yield: 35%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.33 (s, 2H), 0.30 (s, 18H).

3,4-Diphenyl thiophene S-oxide (23c).[20] Yield: 25%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (dt, 2H, J = 7.6 Hz, 0.8 Hz), 7.29 (t, 4H, J = 7.6 Hz), 7.06 (dd, 4H, J = 7.2 Hz, 0.8 Hz), 6.03 (d, 2H, J = 0.8 Hz).

3,4-Dibenzyl thiophene S-oxide (23d).[11] Yield: 18%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34 (m, 4H), 7.15 (m, 6H), 6.06 (s, 2H), 3.63 (s, 4H).

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CHAPTER V

GENERAL CONCLUSIONS

In the last three chapters mechanistic studies for the deoxygenation of dibenzothiophene oxide (**DBTO**) and thiophene oxides (**TO**) were discussed. The mechanism for the deoxygenation of **DBTO** which was proposed by our group is a unimolecular homolytic cleavage of the S–O bond. Although there is no direct evidence for this mechanism, all indirect observations support this hypothesis. In the first two chapters more evidence was provided to reinforce this unimolecular mechanism.

Dibenzothiophene produces **DBT** and $O(^3P)$ upon photolysis. The assignment of $O(^3P)$ is based on the observation of selective oxidation of different solvents. From the energetic point of view, it is clear that bond breaking is not taking place from the luminescent triplet, since the triplet energy of **DBTO** is much lower than the S–O bond cleavage energy. Hence, it is assumed that the bond breaking process is taking place during the surface crossing that can induce considerable stretch in the S–O bond or from a higher triplet manifold. Heavy atom substitution can cause a significant increase in the spin-orbit coupling, which eventually makes all the S $\leftrightarrows$ T processes faster. This idea was used to check whether higher spin orbit coupling could increase the S–O bond cleavage efficiently. Heavy atom substituted **DBTO**s were synthesized and their photophysical and photochemical properties were studied. 4-Bromo and 4-iodo substituted **DBTO**s showed a 50- and 65- fold increase, respectively, in the phosphorescence quantum yield compared to unsubstituted

DBTO, as expected. This increase in phosphorescence quantum yields can result either from greater efficiency in the formation of the triplet, or from a greater fraction of triplets undergoing emissive decay, or both. Unfortunately, the deoxygenation quantum yields were not as high as expected. 4-Iodo **DBTO** was an ideal candidate for deoxygenation, since it showed a very high quantum yield of phosphorescence. But its potential was not reached due to a secondary photoreaction, which dehalogenated the primary photoproduct, 4-iodo **DBT**, at a much faster rate than the deoxygenation. However, the general trend for the quantum yield of deoxygenation showed the order of iodo > bromo > chloro ~ H. This order is consistent with the proposed mechanism of unimolecular S–O cleavage in which bond stretching is coupled to intersystem crossing. The position of the halogen atom did not affect the quantum yield of deoxygenation significantly, which was concluded from the observation that both 4-bromo and 2-bromo **DBTO**s showed similar quantum yields of deoxygenation. Another compound, 2-acetyl **DBTO**, did not deoxygenate, although it showed an extremely high quantum yield of phosphorescence. This could arise from a very emissive triplet state, which is photochemically inert or from the efficiency of the acetyl group to perturb the coupling between intersystem crossing and deoxygenation.

Although the efficiency of deoxygenation was not very high as expected, the data are consistent with the hypothesis. However, another effort in our laboratory by Ryan McCulla to increase the quantum yield by introducing a heavy atom showed the desired result. Dibenzoselenophene oxide, which is an analogue of **DBTO**, showed about 40 times higher quantum yield of deoxygenation than **DBTO**. In this case the sulfur nucleus of **DBTO** was changed to selenium.

The deoxygenation quantum yield of **DBTO** in solvents like cyclohexene and DMSO was already shown to be higher than in other solvents like benzene and acetonitrile. Internal trapping groups were appended to the 4-position of **DBTO**, with the expectation that they would form internally trapped products and they would increase the quantum yield of deoxygenation. Among the substituted compounds, 4-allyl and 4-thiomethyl **DBTO**s showed the best results. Both of these two compounds produced internally trapped products and showed higher quantum yields of deoxygenation. The alternative reactivity of 4-(methylthiomethyl) due to benzylic-type cleavage prevented the use of this compound to demonstrate whether the additional methylene would increase the trapping efficiency in that series.

Acetonitrile and benzene acted differently as solvents for the photolyses. For some **DBTO** derivatives, an internally trapped product was observed in benzene but not in acetonitrile. This could be due to solvent viscosity, dipole moment, or the involvement of multiple excited states. At this time none of these possibilities can be eliminated, and further experimental and computational studies are required to address this issue.

Four differently substituted stable thiophene-*S*-oxides were synthesized and photolyzed. Among these four compounds 3,4-dibenzylthiophene-*S*-oxide was the least stable. But careful handling and storage of this compound made it stable enough to investigate its photochemical reaction mechanism.

The photolysis result of 2,5-bis(trimethylsilyl)thiophene-*S*-oxide is promising, although it is too early to draw any conclusions from it. Photolysis in benzene shows at least a 14-fold increase in the quantum yield of deoxygenation. However, we cannot rule out the possibility that the electronic effect exerted by the silyl group influences the photochemistry.

2,5-Di-*tert*-butylthiophene-*S*-oxide produced the corresponding furan, which is similar to the results already published. The other sulfoxides that have been successfully synthesized gave complex product mixtures. 3,4-Diphenylthiophene-*S*-oxide produced the corresponding furan as a minor product along with other unknown products. The major unknown product had the same mass as the corresponding thiophene. It is possible that the sulfoxide deoxygenated under the photolysis conditions, and the preliminary photoproduct, the corresponding thiophene underwent isomerization. At the same time, direct conversion from the sulfoxide to an unknown product also cannot be ruled out. Control reactions and full characterization of the product mixture are required to shed more light on this mechanism. For 3,4-dibenzylthiophene-*S*-oxide the quantum yield of decomposition is very high (>1) implying that there could be some kind of chain reaction responsible.

The results obtained during this project support the unimolecular 'S-O' cleavage mechanism in the **DBTO** systems. However, it is too early to draw an analogy between the deoxygenation of thiophene-*S*-oxide systems and **DBTO** systems. From the results it is clear that the photochemistry of thiophene-*S*-oxides is not restricted to the 'S-O' bond cleavage reaction and is highly substituent dependent.

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