

Photochemistry of thiophene-S-oxide derivatives

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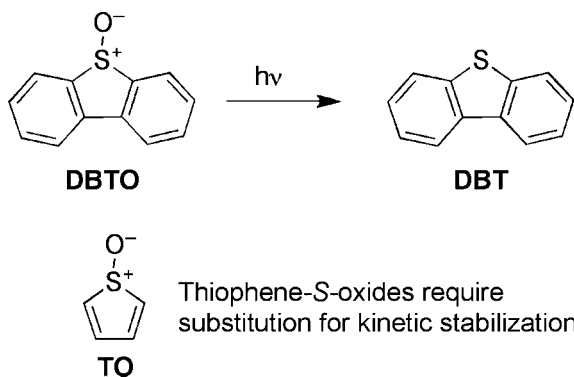
Photolysis of substituted thiophene-S-oxides in solution results in the formation of either the corresponding thiophene or furan, in addition to uncharacterized materials. No good rationalization is available for the choice of which pathway may predominate, but it is demonstrated that the photolysis of 2,5-bistrimethylsilylthiophene-S-oxide produces O(³P) in the same manner as the well-established photolysis of dibenzothiophene-S-oxide. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

The photochemical deoxygenation of dibenzothiophene-S-oxides (DBTOs) to dibenzothiophenes (DBTs) and the corresponding reactions of thiophene-S-oxide (TO) derivatives has a history going back into the 1970s, when first reported by Gurria and Posner.^[1] Deoxygenation of other sulfoxides is known,^[2–4] but it appears that the cases with the greatest chemical yield are generally limited to those in which the sulfur atom resides within a formal thiophene ring.



In 1997, we reported a mechanistic study on DBTO photolysis, in which we suggested that the primary mechanism for photochemical deoxygenation of DBTO was direct dissociation of the molecule to DBT and atomic oxygen, O(³P).^[5,6] This proposal was based mainly on experiments that were thought to exclude other mechanisms – including transient dimer formation and hydrogen abstraction – and on the observation of oxidized solvent in a pattern that seemed appropriate for triplet atomic oxygen. For example, benzene is oxidized to phenol and alkanes are hydroxylated with some selectivity. Although the chemical yield of DBT is high, the photochemical efficiency is poor and subject to solvent and wavelength effects. More recent work on DBTO derivatives from our laboratories has shown that solvent effects in the quantum yield were due to solvent functionality,

rather than polarity, viscosity or other ‘physical’ parameters.^[7] The solvents and substituents that led to higher quantum yields contained functionalities that shared in common a high reactivity with O(³P). Other workers showed that the reactivity of the oxidizing species followed an electrophilic trend in the oxidation of sulfides and alkenes that was consistent with known reactivity from gas phase chemistry.^[8,9]

We believed that DBTO or a related derivative would make an excellent source for flash photolysis experiments and/or other work in which photochemical release of O(³P) was desired, but this was hampered by the low quantum yield (generally < 0.01). Thus, we began to look for ways of increasing the quantum yield of deoxygenation. One successful approach was to substitute Se for S, making the corresponding selenoxide.^[10] A much more modest degree of success was found with heavy atom substitution on the arene.^[11]

A much earlier hypothesis, though, was that derivatives of TO might be particularly good at deoxygenation because of their lower S—O bond dissociation enthalpies^[12,13] and higher excited state energies (Table 1). (A potential flaw in this reasoning is the low triplet energy of cyclopentadiene, which might reasonably be used as a first estimate for the triplet energy of TO.) This made them an attractive target, even though the anticipated absorption spectrum took them out of the range that might be useful with a 355 nm laser line.^[14] An important issue, however, was that TO derivatives must be substituted with relatively bulky groups to kinetically stabilize them against dimerization. Furthermore, it was only in the mid 1990s that the synthesis of TO derivatives became practical.^[15,16]

In work unpublished from our laboratories, save for a PhD dissertation,^[17] we made the observation that photolysis of 2,5-diphenylthiophene-S-oxide did yield the corresponding

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Table 1. Relevant energies for thiophene sulfoxides

	S–O bond dissociation energy, kcal/mol	E_S , kcal/mol	E_T , kcal/mol
DBTO	73 ^a	ca. 85 ^b	ca. 60 ^b
TO	61 ^a	78.6 ^c	ca. 59 ^d

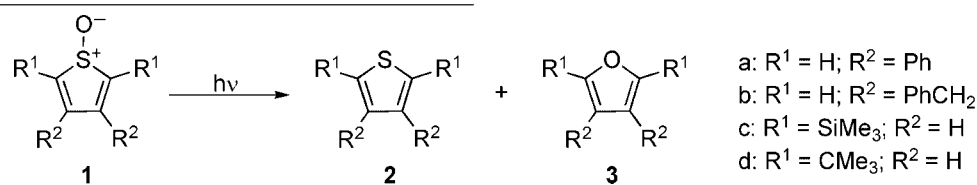
^a Reference[13].
^b Reference[56].
^c Apparent 0,0 band from absorption spectrum of **1c** (this work).
^d Triplet energy of cyclopentadiene.

sulfide in low quantum yield, along with other products. Since we understood that the phenyl groups also would affect the chromophore and we were also interested in doing computational chemistry on the system, we did not pursue this TO derivative further. However, we also observed at this time that photolysis of 2,5-di-*t*-butylthiophene-*S*-oxide resulted in the surprising formation of the corresponding furan.^[17] We were thus relieved and pleased to see the work of Thiemann *et al.*,^[18,19] in which they more thoroughly documented this transformation. They have recently elaborated these studies with several more sulfoxides.

Thiemann has recently reviewed his group's work in this area,^[20] but a short synopsis is useful here.

Furan formation

Certain TO derivatives produce the corresponding furan on photolysis, in minor to major yield, depending on the structure. There is not yet a good rationalization for the choice of which sulfoxides produce the furan. Among them are 2,4- or 2,5-di-*t*-butylthiophene-*S*-oxide and tetraphenylthiophene-*S*-oxide. No firm mechanism can yet be established. However, Thiemann has



proposed a mechanism passing through the cyclic oxathiin isomer (Scheme 1, illustrated for 2,5-di-*t*-butylthiophene-*S*-oxide).^[20] The first step, α -cleavage, is a mechanism that is well established in sulfoxide photochemistry.^[3,4] There is ample precedent for analogous dithiins photochemically desulfurizing to produce thiophene.^[21–23] There is nothing published that distinguishes whether a second photon is required for desulfurization of TOs, but the general pathway of going through the oxathiin seems quite reasonable.

Deoxygenation

Nearly every sulfoxide examined by Thiemann, save 2,5-di-*t*-butylthiophene-*S*-oxide, undergoes deoxygenation to form the

thiophene in some measurable yield.^[20] Those that produce other products (e.g., the furan) can be induced to yield mainly the thiophene by addition of several equivalents of an amine, triphenylphosphine or an electron rich thiol. This may be mechanistically related to the observation of electron-transfer-sensitized photoreductions of a number of sulfoxides.^[24,25]

'Benzyl' functionalization

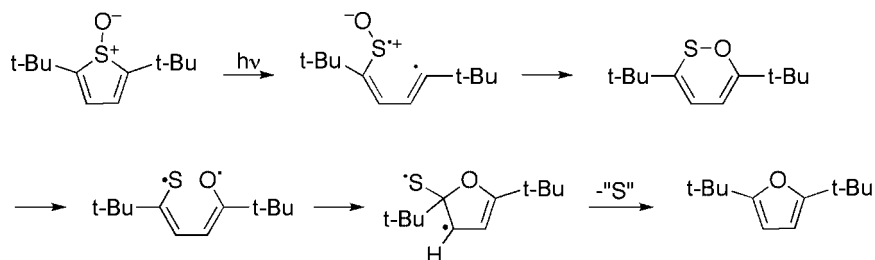
Thiemann examined a series of TO derivatives that contained methyl groups in the 2 and 5 positions. In the absence of hydroxylic solvent, the thienyl alcohol and/or thienyl ether is observed as part of the product mixture; ethanol was used to form the ethyl thienyl ether in at least one case.^[19,20,26] This reactivity was attributed to secondary reactions between water or an alcohol and the corresponding 2-methylene-3*H*-thiophene-*S*-oxides or 2-methylene-5*H*-thiophene-*S*-oxides, though neither of these intermediates has been observed directly.

In that the 'benzyl' functionalization was avoidable by not using certain substituents, we undertook a study of some of these reactions that was meant to be more mechanistic in nature and that we report here. We now report the photochemistry of TOs **1a–1c**, which shows both deoxygenation and the furan formation without the complication of benzyl functionalization. We also report a brief computational investigation on the mechanism of furan formation.

RESULTS

We wished to study the photochemistry of a series of thiophene oxides that did not include the potentially complicating substituents of Br (photochemical cleavage) or 2,5-dimethyl (isomerization). Ideal substrates seemed to be 3,4-di-*t*-butylthiophene-*S*-oxide or 3,4-di-neopentylthiophene-*S*-oxide, which are prepared by oxidation of the appropriate thiophene. The former of these has been prepared (via a McMurry coupling for the key cyclization step)^[27–30] and its chemistry has been

reported.^[31–33] We do not dispute these reports, but in our hands, the McMurry coupling was extremely problematic for this substrate and did not result in synthetically useful product mixtures.^[34] We had similar difficulties preparing the di-neopentylthiophene and were also unsuccessful in coupling neopentyl groups to dibromothiophene via the Kumada method. A second synthetic procedure toward di-*t*-butylthiophene, in which 2,5-dibromothiophene was subjected to Friedel-Crafts alkylation with *t*BuCl and AlCl₃, followed by debromination, resulted in the isolation of 2,5-di-*t*-butylthiophene.^[35] Ultimately, we prepared and studied the photochemistry of three sulfoxides: 3,4-diphenylthiophene-*S*-oxide, **1a**, 3,4-dibenzylthiophene-*S*-oxide, **1b**, and 2,5-bis(trimethylsilyl)thiophene-*S*-oxide, **1c**. These sulfoxides were prepared by the oxidation of the corresponding



Scheme 1.

thiophenes, whose individual preparations are described in the Experimental section, by oxidation by *m*CPBA in the presence of BF_3 .^[15,29]

Direct photolysis

Table 2 summarizes the results obtained on photolysis of sulfoxides **1a**, **1b**, and **1c**. Photolyses were carried out in Ar-flushed solutions with initial concentrations of 1–5 mM. Modest yields of **2** or **3** were obtained. Neither identifiable products were obtained, nor were any other soluble products ever formed as major products. The quantum yield for loss is defined as the observed quantum yield for all processes leading to the loss of the respective starting material.

Photolysis of 3,4-diphenylthiophene-S-oxide in either acetonitrile or methanol resulted in modest amounts of furan (**3a**) formation, near 22%. Yields were determined by ^1H NMR and GC. No thiophene was observed, regardless of the degree of conversion. Several minor, unidentifiable products were formed. At least some appeared to be isomeric with **3a**, in that they had aromatic protons in the NMR, differing chromatographic

retention times and apparent masses identical to **3a** (GCMS). In methanol, an unidentified precipitate was formed if solutions of *ca.* 20 mM initial concentration were photolyzed.

Photolysis of dibenzyl derivative **1b** also led to furan (**3b**) in low yield without observation of the thiophene. A small quantity of bibenzyl was detected in all three solvents, but no other identifiable compounds were noted.

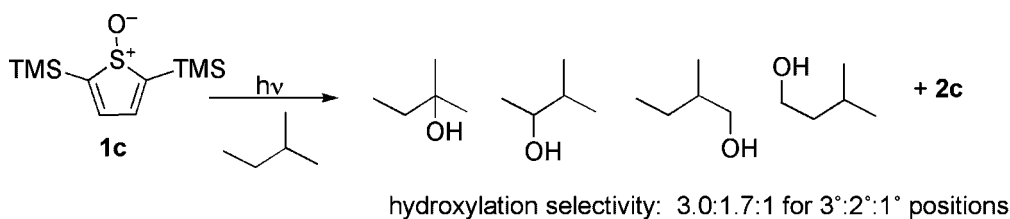
In contrast to **1a** and **1b**, photolysis of 2,5-bis(trimethylsilyl)thiophene-S-oxide (**1c**) led to deoxygenation (**2c**) to the exclusion of furan formation. Consistent with our observation on DBTO,^[5] excitation at a shorter wavelength increased the quantum yield of sulfide formation.^[36] No product corresponding to the mass or ^1H NMR of **3c**^[37] was obtained.

In order to probe for $\text{O}(^3\text{P})$ formation, a suitable probe that did not absorb the incident light was sought; alkane hydroxylation seemed ideal. Photolyses of **1c** or DBTO in 2-methylbutane led to very similar quantities of alkane hydroxylation products. Adjusting for the number of hydrogens, a hydroxylation selectivity of 3.0:1.7:1 was observed for tertiary:secondary:primary positions (Scheme 2). This agrees well with our previously reported result for DBTO.^[6]

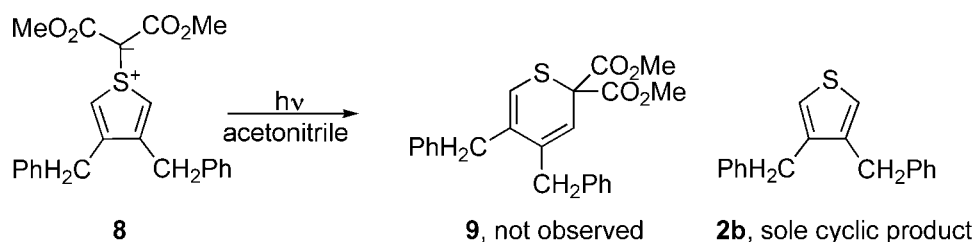
Table 2. Results of direct photolysis of thiophene sulfoxides^a

Sulfoxide	Solvent	λ_{exr} nm	Φ_{Loss}	Yield 2 , (%)	Yield 3 , (%)
1a	CH_3CN	300	0.006	0	22
	CH_3OH	300	0.0072	0	23
1b	CH_3CN	325	0.064	0	17
	<i>i</i> PrOH	325	0.042	0	17
	CDCl_3	325	0.021	0	12
1c	CH_3CN	260	0.080	26	0
	CH_3CN	325	0.11	12	0
	C_6H_6	325	0.13	17	0

^aQuantum yield is for loss of starting sulfoxide by all processes. Yields are relative to the consumed starting material.



Scheme 2.



We wished to probe the mechanism for furan formation. As suggested by Thiemann, a mechanism for formation of the furan can be elaborated from the now well-documented mechanism for thiophene formation from dithiins.^[21–23] Substituting oxygen for sulfur results in the pathway illustrated in Scheme 3. Although this varies from the Thiemann pathway shown in Scheme 1, it shares in common the key oxathiin intermediate. Certainly troubling in both pathways is the unspecified mechanism for loss of sulfur in the final step, but this process is well documented for thiiranes.^[21–23] Our primary interest was thus in the initial photochemical step(s) postulated to provide the isomers of **5**.

We sought direct evidence for the oxathiin intermediate. Photolyses of **1a** were carried out at $-20\text{ }^{\circ}\text{C}$ in CD_3CN to low and then higher conversion, with analysis by NMR at the same temperature, to try to observe any evidence for the oxathiin **5a**. The only identifiable protons, aside from starting material, were attributable to **3a**, the furan. No protons from any asymmetric compounds, which would display ^1H - ^1H coupling, were observed. The low-temperature reaction was repeated with O_2 saturation instead of Ar saturation in an unsuccessful attempt to trap intermediates in the formation of the furan by oxidation.^[10] (See below for a precedent for O_2 as a trap for an intermediate analogous to this with selenoxide photochemistry.) If the unstable oxathiin **5a** had been formed, there would have been potential to trap it as the more stable sultine. No difference was observed between this and the Ar-saturated case.

Photolysis of **1a** was carried out in a perdeuterated ethanol/methanol glass at 77 K in an NMR tube. The frozen glass was warmed to $-50\text{ }^{\circ}\text{C}$ in the NMR probe, and analysis was carried out. Again, the only identifiable product was the furan **3a** at both $\sim 5\%$ conversion and complete conversion.

We have recently shown^[38] that malonate *S,C*-sulfonium ylides of thiophene generate carbenes, but we thought there might be a chance of observing an isomeric product analogous to the proposed oxathiin with the correct substitution pattern. We chose **8**, based on the sulfoxide results. However, irradiation of **8** in acetonitrile resulted only in thiophene **2b** and carbene-derived products.^[38] The thiophene was formed nearly quantitatively relative to consumption of **8**. NMR indicated the presence of carbene-solvent adduct; aside from protons attributable directly to **2b**, neither alkenyl nor aromatic hydrogens were observed. By HPLC analysis, the only benzyl-containing product was **2b**.

Computations regarding furan formation

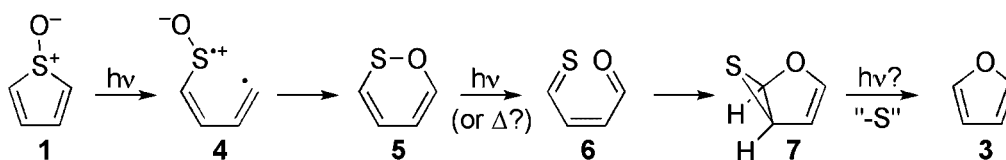
The inability to isolate intermediates as illustrated in Scheme 3 does not necessarily eliminate this general pathway for the formation of furan. In particular, if the intermediates are destroyed more rapidly than they are formed under the reaction conditions, they will never accumulate. We thus undertook a brief computational study to investigate the relative energies of the various isomers.

Computations were carried out at the B3LYP and MP2 levels of theory with the GAMESS^[39] suite of programs. Geometries were optimized with the 6-31G(d) basis set, and the respective vibrational matrices showed that each structure was a minimum. It is well known that fairly large basis sets that contain tight d polarization functions are required to get good relative energies for the oxides of sulfur^[13,40–52] We thus used the aug-cc-pV(T+d)Z basis set to obtain single point energies at the so-obtained geometries (i.e., MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d) or B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d)). We did not attempt to find transition structures connecting the compounds.

The free energies (*G*) in Fig. 1 include zero point energies and a temperature correction to 298 K. The energy of the episulfide (**7**) is arbitrarily set to zero. In Fig. 1a, the energies of the sulfoxide, oxathiin, and episulfide are all given. Additionally, the isomeric epoxide is shown.

Three conformations for compound **6** were obtained. The lowest energy conformation had both the $\text{C}=\text{S}$ and $\text{C}=\text{O}$ rotated away ("exo") from the internal pi bond. The "O-exo" conformation has the sulfur atom canted out of plane by $\sim 15^{\circ}$ and the highest energy. The S-exo conformation was approximately planar, and the di-exo conformation was rigorously planar. For oxathiin, the O and S are displaced above and below the plane of the carbons, as expected. Figure 2 illustrates the CC, CS, CO, and SO bond lengths calculated at the MP2/6-31G(d) and B3LYP/6-31G(d) levels.

By way of comparison, three corresponding structures corresponding to the $\text{C}_4\text{H}_4\text{S}_2$ energy surface were optimized and their energies were calculated in the same way. They are plotted on the same energy scale in Fig. 1b. The thiosulfoxide is not a relevant structure. The larger $\text{C}=\text{S}$ substituent in the acyclic isomer makes only the single diexo conformation a relevant minimum, and of course, there is not a second bicyclic analog, since both heteroatoms are sulfur.



Scheme 3. A potential pathway for furan formation from thiophene oxides

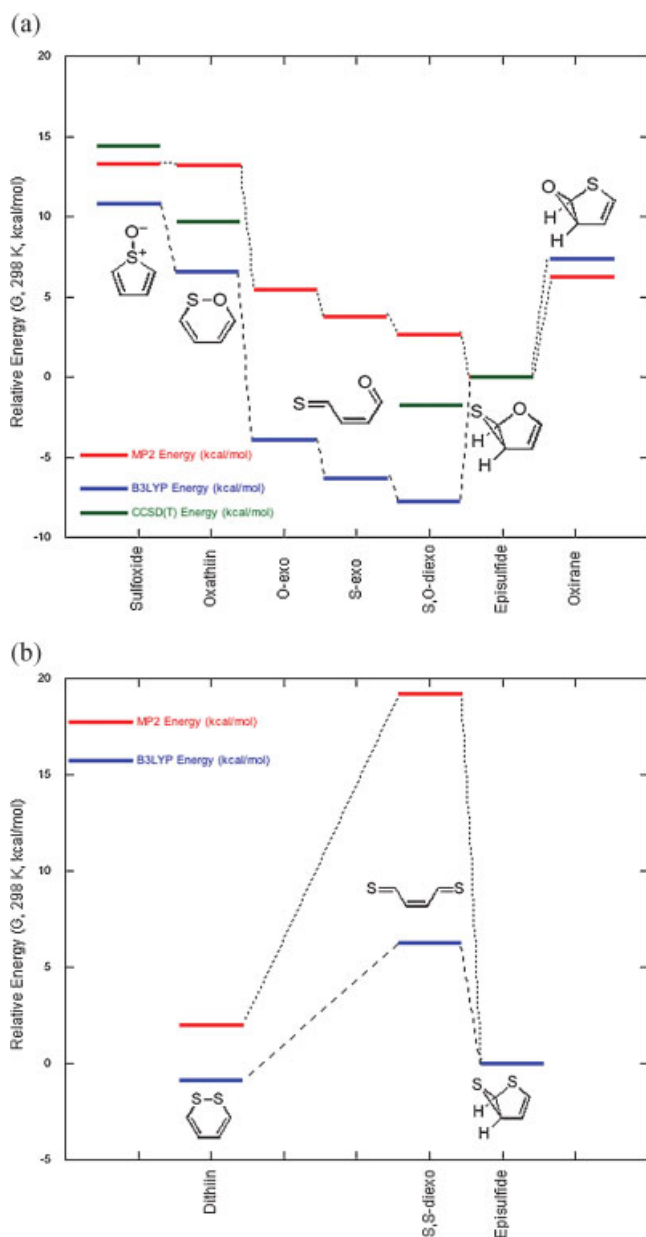


Figure 1. Calculated free energies for isomeric structures of (a) C₄H₄OS and (b) C₄H₄S₂. Energies are MP2/aug-cc-pV(T + d)Z//MP2/6-31G(d), CCSD(T)/aug-cc-pV(T + d)Z//MP2/6-31G(d), or B3LYP/aug-cc-pV(T + d)Z//B3LYP/6-31G(d) with ZPE and 298K temperature corrections taken from MP2/6-31G(d) or B3LYP/6-31G(d) vibrational calculations, as appropriate

As can be seen in Fig. 1a, the relative energies of the C₄H₄OS species differ dramatically, depending on the computational method. As a check against great sensitivity to the geometries, additional single point energies were calculated at the B3LYP/aug-cc-pV(T + d)Z//MP2/6-31G(d) level. Only small differences between these energies and those obtained at B3LYP/aug-cc-pV(T + d)Z//B3LYP/6-31G(d) were observed, so the qualitative picture in Fig. 1 would not change. Similarly, the use of Jensen's *a*-PC2 basis set (i.e., B3LYP/*a*-PC2//B3LYP/6-31G(d)), specifically optimized for use in density functional applications,^[53] gave very similar results to the B3LYP results with the aug-cc-pV(T + d)Z calculations. Qualitatively, the HF//

aug-cc-pV(T + d)Z//MP2/6-31G(d) energies, that is, not including any correlation energy, followed the same pattern as the B3LYP calculations, rather than the MP2 calculations. (All of the absolute and relative energies are given in the Supporting Information.)

This kind of huge discrepancy between B3LYP and MP2 calculations is not expected. Moreover, the kind of bonding involved in the various molecules in the series is so different that these isomerizations are far from isodesmic reactions. Any method-dependent errors that are sensitive to functional groups will be highlighted, rather than cancelled out. We thus face the reality that at least one of these two methods is highly flawed for this set of compounds. As a check for the MP2 data, we examined the natural orbital occupation numbers, and all were in the natural range of 0–2.

We are unaware of a similar straightforward diagnostic for troublesome B3LYP calculations. Furthermore, while many density functionals are available, there is no straightforward, rational sequence that one can follow to ensure an improvement of the quality of the calculations. However, it is now fairly well accepted that the sequence of HF → MP2 → CCSD(T) is a rigorously improving sequence of methodology for single-reference problems. While CCSD(T) computations are expensive, we felt the need to try to resolve the strong disagreement between the B3LYP and MP2 methodologies.

Thus CCSD(T)/aug-cc-pV(T + d)Z//MP2/6-31G(d) calculations^[54] were run on the episulfide and dioxo conformation of **6** as well as on **1** and **5**. The temperature correction obtained from the MP2 calculations was added to obtain the G(298 K) values. The CCSD(T) energy differences, which are clearly the most reliable of the three types obtained, remarkably reflect almost the average of the widely differing MP2 and B3LYP values. As can be seen in Fig. 1 and Table 3, the relative energy of the dioxo ring-opened compound is slightly below that of the episulfide. The relative energies of the conformers of **6** were not explored by the high level calculations, as the pattern was in agreement in both lower level methods.

Sensitized photolysis

Benzophenone-sensitized photolysis of **1a** or **1b** in acetonitrile resulted in a complex product mixture that contained neither the corresponding thiophenes nor furans. No isolable products were identified. Both low and high conversion experiments were run. The benzophenone concentration was approximately 30 mM, near the minimum required to ensure absorption of at least 99.9% of the light by benzophenone in the presence of 0.5 mM of the respective sulfoxide.

Benzophenone-sensitized photolysis of **1c** was not practical because the absorption spectrum of **1c** extended too far to the red to exclusively irradiate benzophenone.

DISCUSSION

Deoxygenation

Of the three sulfoxides examined, only **1c** showed significant yields of deoxygenation, that is, the thiophene **2c**. The observed hydroxylation selectivity of 2-methylbutane is quite similar to that we reported previously for DBTO,^[6] and we thus tentatively conclude that the mechanism of deoxygenation is the same as that for DBTO, that is, direct dissociation to form O(³P). Although the quantum yield is higher than for DBTO, the chemical yield is

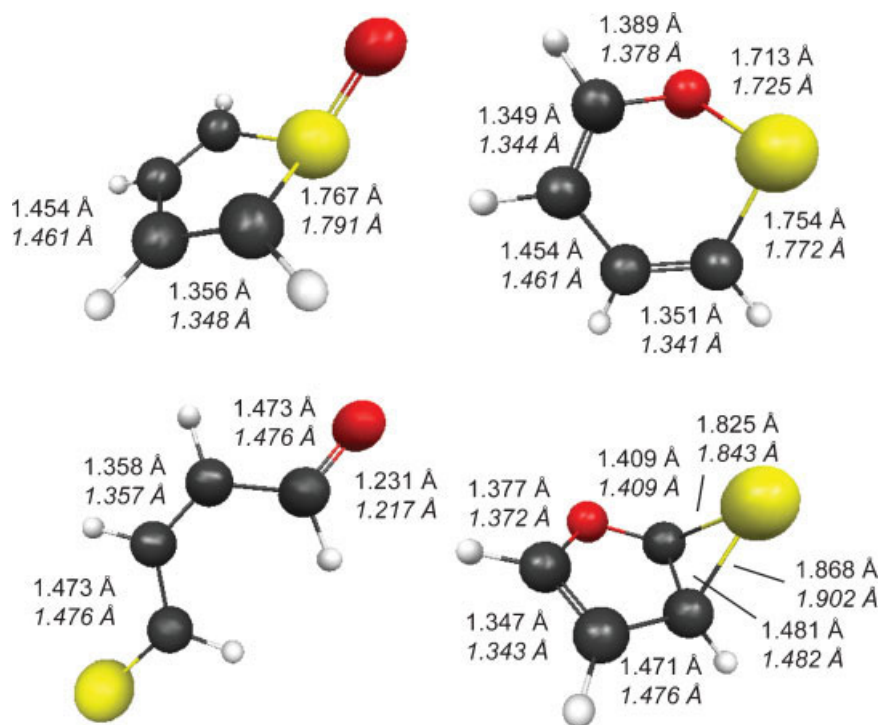


Figure 2. Optimized geometries for C_4H_4OS isomers. Bond lengths shown in normal text are from MP2/6-31G(d) and those in italics are from B3LYP/6-31G(d) calculations. CH bond lengths are not illustrated

poor enough so that **1c** is probably not an especially useful compound for the intentional generation of oxygen atoms.

A full study on the sensitized deoxygenation of DBTO is being reported elsewhere,^[55] but it can briefly be stated that benzophenone-sensitization of DBTO does not produce $O(^3P)$, and the subsequent deoxygenation certainly does not go by the same mechanism as is observed for direct photolysis of DBTO. Thus, particularly considering the low triplet energy of TO we expect, it does not come as a surprise that no evidence of unimolecular deoxygenation was found on sensitization of either **1b** or **1c**. (We routinely examine sulfoxides for phosphorescence to determine the triplet energies, but it is only the exceptional case in which any is observed, e.g., DBTO itself or methanesulfinylpyrene.^[56,57])

Thiemann has reported^[20] that addition of easily oxidizable substrates (e.g., amines and sulfides) to solutions containing TOs increases the yield of thiophene after photolysis. This effect

occurs regardless of whether direct photolysis in neat solvent produces mainly furan, thiophene, or other products. The clear implication is that there is a second reduction mechanism in those instances. We believe that it is quite likely that this is related to the electron-transfer-mediated sulfoxide reduction previously demonstrated by Kropp and ourselves.^[24,25] Thus, while of interest, we did not believe it was critical to our current investigation to reproduce such results for these particular substrates.

Furan formation

We have assumed from the beginning that photochemical furan formation from thiophene-based sulfoxides is “unimolecular,” in that it involves only a single TO molecule. That assumption is due to two lines of thought. First, although we do not report a systematic study here, we have never seen evidence for a

Table 3. Relative energies of C_4H_4OS isomers at various computational levels^a

G_{rel}^{298K}	1	5	6 O exo	6 S exo	6 di exo	7	Oxirane ^b
B3LYP/aug-cc-pV(T + d)Z//B3LYP/6-31G(d)	10.8	6.6	-3.9	-6.3	-7.7	0.0	7.4
MP2/aug-cc-pV(T + d)Z//MP2/6-31G(d)	13.3	13.2	5.5	3.8	2.7	0.0	6.3
HF/aug-cc-pV(T + d)Z//MP2/6-31G(d)	16.4	7.8	-5.5	-8.1	-9.4	0.0	6.8
B3LYP/aug-cc-pV(T + d)Z//MP2/6-31G(d)	10.7	6.6	-3.7	-6.0	-7.5	0.0	5.9
CCSD(T)/aug-cc-pV(T + d)Z//MP2/6-31G(d)		9.7			-1.7	0.0	

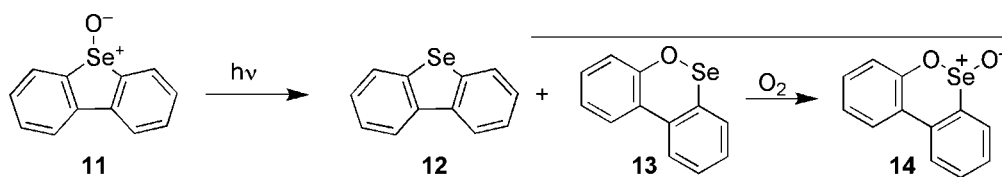
^a All energies in kcal/mol. Unscaled ZPE and temperature correction to 298 K, calculated at MP2/6-31G(d) [or B3LYP/6-31G(d) for the density functional calculations] are included.

^b Oxirane refers to the structure obtained by exchanging the O and S in structure **7**.

concentration-dependence on a product distribution. We are confident that under our conditions, deoxygenation is unimolecular (based on the analogous studies of DBTO). If furan formation involved two TO derivatives, then we would likely have seen more thiophene formation at low initial concentrations and more furan formation at higher concentrations, or perhaps a conversion-dependent product distribution. Nothing of the sort has been observed in the concentration range of *ca.* 10^{-4} – 10^{-2} M. The second line of reasoning is that the reaction would have to be rather complex. The initial step might be oxygen atom transfer, but this should lead to the observation of a thiophene derivative in the mixture. The initial step might also be electron transfer (single-electron disproportionation), but again, the best analogous evidence is that this should ultimately lead to observation of thiophene derivative as part of the product mixture. This said that the large amount of uncharacterized product material implied by the low yields does leave the door at least a little open to such a possibility. Nonetheless, we will proceed further with the assumption that the initial steps of photochemical furan formation do not require a second TO nucleus.

Given a fundamentally unimolecular initial step, the formation of the furan due to irradiation of thiophene oxides seemingly “must” proceed through the oxathiin in the sense that it is hard to come up with a sensible alternative. The known chemistry of the dithiins^[21–23] that leads to thiophenes seems quite analogous. In the current sulfoxide-based case, the initial bond C—O bond formation by way of the oxathiin **5** seems inescapably logical and inescapably photochemical in origin, due to α -cleavage and isomerism.

However, direct evidence for **5** is lacking to the best of our knowledge. The closest analog of which we are aware is our own assignment of the analogous structure during the photolysis of dibenzoselenophene-*Se*-oxide, **11**.^[10] In addition to deoxygenating (**12**) on direct irradiation, **11** yields an isomeric compound whose ¹H NMR is indicative of an asymmetric compound with two aromatic ABCD spin systems and whose mass is the same as **11**. We assigned the structure **13** to that compound, in part due to chemical deduction, but also in part because the presence of O₂ in the sample converted that compound (assigned to **13**) to another compound. The new product also had two aromatic ABCD ¹H spin systems, but had a mass 16 g/mol higher than that of **11** and **13** and was assigned to the sultine analog **14**.



Given the room-temperature existence of certain dithiins, we believed that observation of the oxathiin might be possible, though we failed in that attempt. However, it is possible that the strategy was doomed to fail to begin with because of greater absorption by **5** (which would prevent the accumulation of **5**, regardless of temperature). Dithiins are characterized by a low energy absorption in the visible, assigned to an $n \rightarrow \sigma^*$ band.^[58,59] The lamp systems used by the Thiemann group and ourselves in the great majority of experiments provide relatively broad irradiation, which implies that a compound with an absorption to the red of the starting material is likely to absorb light efficiently

under the experimental conditions. It is possible that narrow irradiation at a well-chosen wavelength (where absorption by the starting sulfoxide is much greater than that of **5**) could allow for accumulation of **5**, but unfortunately, we do not know the absorption spectrum of **5**, a requirement to design that experiment properly.

The carbon analog **8** would have yielded **9**, which should not have had extra low-energy bands of the dithiin sort. However, it simply does not undergo any process besides loss of the carbene to a substantial degree.

We thus sought further information on the relative stabilities of the structures in Scheme 3 by computational methods. In principle, the postulated ring opening from **5** to **6** could be thermal, but it is photochemical in the dithiin cases.^[21–23] However, formation of **6** involves the formation of a C=O pi bond in lieu of a C=S pi bond for the dithiin analog. Given basic knowledge of the relative strengths of C=S versus C=O pi bonds and S—S versus S—O sigma bonds,^[51] it seemed reasonable to expect that the conversion of **5** into **6** would be more exergonic than the corresponding opening of a dithiin to a dithial. This expectation is clearly borne out in the computational results, though the latter are hardly quantitatively definitive.

Although the conflict between the MP2 and B3LYP calculations cannot be explained fully at this time, there is still worthwhile information that can be extracted. The CCSD(T) calculations clearly show that the ring opening of the oxathiin to **6** is exothermic by about 10 kcal/mol. Assuming this general pathway is followed, we cannot at this time distinguish secondary photolysis of the oxathiin or a low-barrier thermal process. The relative stability of these isomers is apparently reversed in the case of the dithiin, and thus it is probably not surprising that a limited number of simple dithiins have been observed at room temperature, while no simple stable oxathiins are known.

The transformation of **6** into **7** is endergonic, according to the CCSD(T) calculations, by a couple of kcal/mol, starting from the lowest energy conformation of **6**. The process will be energy-neutral or slightly exergonic from the initial conformation of **6** formed from **5**. However, the final equilibrium favoring formation of thiophene is almost certainly driven by an unspecified, but exergonic desulfurization mechanism.

The lack of observation of any derivative of **6** or **7** at low temperature suggests (but does not prove) that the conversion of derivatives of **6** to furans is photochemical. The bulky

substituents will surely change the relative energies of **6** and **7** a little bit,^[60] so it is hard to say which of these two will be of lower energy. Regardless, it should also be noted that desulfurization must also take place at low temperature.^[61] (It should also be pointed out that the “-S” notation is commonly used in this literature, but should not be taken to imply that atomic sulfur is necessarily produced.)

Clearly, a more extensive computational investigation is required to give convincing quantitative data on these reactions, and we did not pursue the transition state between **5** and **6** at this time. However, what can be concluded is that (1) the thermal

barrier to ring opening will certainly be lower for the oxathiin than for the dithiin; and (2) if the product of photochemical ring opening of **5** is mainly determined by product stability, the quantum yield of oxathiin ring opening should also be higher than that of dithiin.

CONCLUSIONS

Although we have demonstrated a single thiophene-based sulfoxide (**1c**) that does undergo deoxygenation with a higher quantum yield than does DBTO, this compound would appear to have limited utility as an O³P precursor due to its low chemical yield and uncharacterizable byproducts.

More notable, though, in the sum of both this work and that of others in this field is the unpredictability of the major isolable product: the corresponding thiophene or the furan (except, perhaps, in the instances with a methyl group in the 2-position^[20] due to the intervention of a third major process). With the transformation of the sulfoxide to a *S,C*-sulfonium ylide, however, we have seen no process other than the analog of deoxygenation, that is, carbene formation.^[38]

Thus, at this stage we are left to tentatively conclude that the competition between furan formation – which we presume to begin with the α -cleavage event – and deoxygenation compete with one another based on closely spaced energy surfaces in the relevant excited states. Until a more detailed understanding of the subtleties of the effect of molecular structure on those dynamics can be obtained, it is likely that the finding of furan or thiophene formation from the photolysis of thiophene sulfoxides will remain empirical.

EXPERIMENTAL

Materials

Unless otherwise noted, all solvents for photochemical experiments were of the highest purity commercially available, and all reagents were used as received.

Thiophenes

3,4-Diphenylthiophene (**2a**),^[62] 3,4-Dibenzylthiophene (**2b**),^[63,64] and 2,5-bis(trimethylsilyl)thiophene (**2c**)^[65] were prepared as previously described.

Thiophene S-oxides: general procedure^[15,29]

To a solution of substituted thiophene (1 eq.) in dry dichloromethane was added boron trifluoride-diethyl etherate (4 eq.). The solution was stirred at -20°C for 10 min. Then *m*CPBA (1 eq.) in dry dichloromethane was added to the stirred solution drop-wise. The solution was stirred at -20°C under argon for another 2 h. Saturated sodium bicarbonate solution was then added to the reaction mixture and stirred for half an hour at room temperature. The aqueous layer was extracted twice with methylene chloride and the organic layer was washed with water and brine. The solution was dried over magnesium sulfate and concentrated in vacuo. The sulfoxide was isolated by chromatography using 30% ethyl acetate in hexane. 3,4-Diphenylthiophene-*S*-oxide (**1a**): Typical yield 25%. ¹H NMR (CDCl₃, 400 MHz): δ 7.39 (dt, 2H, $J=7.6$ Hz, 1.6 Hz), 7.29 (t, 4H,

$J=7.6$ Hz), 7.06 (dd, 4H, $J=7.2$ Hz, 1.6 Hz), 6.63 (d, 2H, $J=0.8$ Hz). ¹³C: δ 145.2, 131.4, 130.2, 128.7, 128.6, 127.6; MS (TOF, EI) *m/z* 236.07; 3,4-Dibenzylthiophene-*S*-oxide (**1b**): Typical yield 18%. ¹H NMR (CDCl₃, 300 MHz): δ 7.34 (m, 4H), 7.15 (m, 6H), 6.06 (s, 2H), 3.63 (s, 4H). ¹³C: δ 146.4, 135.4, 129.3, 129.1, 128.1, 127.8, 34.9; MS (TOF, EI) *m/z* 264.10; 2,5-Bis(trimethylsilyl)thiophene-*S*-oxide^[15] (**1c**): Typical yield 45%. ¹H NMR (CDCl₃, 300 MHz): δ 6.83 (s, 2H), 0.36 (s, 18H).

Furans

3,4-Diphenylfuran (**3a**) was prepared as described by Fallis.^[66] 3,4-Dibenzylfuran (**3b**) was prepared from 3,4-bis(tributylstannyl)furan^[67] by the method of Yang.^[68]

Dibenzylthiophenium bismethoxycarbonylmethylide (**8**)

In a small vial, 3,4-dibenzylthiophene (204 mg, 0.77 mmol), dimethyldiazomalonate (132 mg, 0.77 mmol) and a rhodium catalyst [Rh(OAc)₂]₂ (2 mg, 0.0045 mmol) were mixed together. The mixture was allowed to stir for 2 days in the dark, open to the air, after which the color changed from an emerald green to a brownish-teal. IR indicated that the diazo compound had been completely consumed. The mixture was washed with hexane to leave behind a dark green precipitate. Another washing with 75% ethyl acetate and 25% hexane removed the residual catalyst, leaving behind a white residue, which proved to be 3,4-dibenzylthiophenium bismethoxycarbonylmethylide (136 mg, 57.4% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.32 (t, $J=7.2$ Hz, 4H), 7.26 (t, $J=7.2$ Hz, 2H), 7.15 (d, $J=7.2$ Hz, 4H), 6.36 (s, 2H), 3.73 (s, 4H), 3.65 (s, 6H); ¹³C NMR: δ 165.8, 149.6, 136.5, 129.1, 128.9, 127.4, 126.4, 51.3, 35.6; MS (EI) *m/z* 394.

Photolyses

Photolyses were carried out by using spectro grade solvents with initial concentration in the range of 1–5 mM and all solutions were purged with Ar to remove O₂, unless otherwise noted. Dodecane was used as an internal standard for GC and dioxane was used as an internal standard for reactions monitored by NMR. Valerophenone was used as the actinometer.^[69] The light source was a 75 W Xe lamp coupled to a monochromator with a cell-holder mounted at the exit. The slit widths allow a linear dispersion of ± 12 nm from the stated wavelength, which was adjusted for each compound to minimize absorption by the products. Samples, held either in 1 cm quartz cells or NMR tubes, depending on the method of analysis, were deoxygenated by flushing with Ar. Stirring was provided either by a small magnetic bar or by constant slow Ar bubbling. Analysis was conducted preliminarily by NMR, and further by HPLC, LCMS, and GC, including GCMS. GC work was limited by the fact that the sulfoxides did not survive the chromatography. Quantification was generally carried out by using HPLC. Mass spectra were obtained to help confirm product identification, using LCMS. Analyses and quantifications of alcohols were carried out by GC. Control experiments showed that all compounds **2a–c** and **3a–c** were photostable under the conditions used.

Some preliminary and low-temperature experiments were carried out by using the broad emission centered at 300 nm from low-pressure fluorescent tubes in a Rayonet mini-reactor from Southern New England Ultraviolet Company.

The photolysis at 77 K was carried out with an initial sulfoxide concentration of 10.1 mM in a 1:9 mixture of perdeuterated

ethanol:methanol solvent mixture. The solution was flushed with Ar in an NMR tube and then plunged into liquid nitrogen in a transparent quartz dewar. The light source was the broadly emitting 300 nm tubes described previously. In separate experiments, after 2–3 min (6 bulbs) or 40 min (8 bulbs), the NMR tube was allowed to warm in the dark to -68°C in an acetone/dry ice bath before being lowered into a pre-cooled NMR probe held at -50°C . Spectra were obtained at -50°C and periodically as the sample was allowed to warm slowly to room temperature. No significant change was observed in the spectrum over this period of time, save for a small change in the chemical shift of the thiophene protons (<0.1 ppm). The short photolysis resulted in an approximate 5% conversion of **1a**, while the longer photolysis converted all of the material. After withdrawal of the sample from the NMR instrument at room temperature, a small quantity of solid material was observed in the high conversion sample, as in the room temperature photolyses in methanol.

Computational methods

All computations were done by using the GAMESS suite of programs^[70] and all structures and orbitals were visualized by using the MacMolPlt^[71] application.

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