

Photochemical generation of electron poor reactive intermediates: Photochemistry of S-alkoxy dibenzothiophenium tetrafluoroborates, N-alkoxy pyridinium perchlorates, and Sulfonium ylides

by

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

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Ames, Iowa
2020

DEDICATION

Dedicated to my mother (Leelavathi Kolattoor),
father (Sudhakar Reddy Kolattoor),
wife (Ramya Theja Mallu), and
my son (Shivank J. Kolattoor)

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ABSTRACT

Photolysis of thiophene ylides such as dibenzothiophene ylide (DBTY) and 2,5-dichlorothiophene ylide (DCTY) provides a route to certain carbenes with adjustable photophysical parameters, in that the absorption spectrum of the precursor and the initial spin population of the carbene can be varied. However, the accumulated thiophene from extensive photolysis can act as a triplet sensitizer leading to the generation of relatively high proportion of triplet carbene. It is demonstrated that dibenzothiophene has this property and 2,5-dichlorothiophene does not.

S-alkoxy dibenzothiophenium and N-alkoxy pyridinium salts are prepared and photolyzed to explore the potential homolytic and heterolytic paths of the photochemical S-O cleavage of the thiophenium salts. The heterolytic path would generate a highly unstable electron-deficient alkyl oxenium ion and the corresponding neutral leaving group. Homolysis would generate an alkoxy radical and the corresponding radical cation of the leaving group. The evidence obtained suggests the homolytic formation of alkoxy radical and radical cation of the leaving group though some fraction of the oxenium and the neutral leaving group cannot be ruled out completely.

CHAPTER 1. GENERAL INTRODUCTION

1.1 Dissertation organization

This dissertation consists of four chapters. Chapter 1 is a general introduction of sulfonium ylides, sulfonium tetrafluoroborates, and pyridinium perchlorates, which includes the nomenclature and a general background on the photochemical pathways of each photochemical precursor based on the literature review.

Chapter 2 is a paper published in the *Journal of Photochemistry and Photobiology A: Chemistry* in 2018 which compares the direct photolysis and dibenzothiophene sensitized photolysis of a dibenzothiophene sulfonium ylide (DBTY) and a 2,5-dichlorothiophene ylide (DCTY) to establish dibenzothiophene that is been accumulated during the photolysis or added to the reaction act as a sensitizer.¹

Chapter 3 discusses the photochemistry of S-alkoxy thiophenium tetrafluoroborates and N-alkoxy pyridinium perchlorates. This project is to investigate whether the sulfur bearing precursors are undergoing photo-heterolysis (generating alkoxy oxenium ion intermediate and a neutral leaving group either DBT or pyridine) or photo-homolysis (generating alkoxy radical and a radical cation of the leaving group DBT). Chapter 4 draws some general conclusions of the previous chapters.

1.2 Nomenclature of Sulfur ylides

Generally, in sulfur compounds, thia- or thio- is used to name the compounds where oxygen has been replaced by sulfur. For instance, if the oxygen in an ether, anisole or phenol has been replaced by sulfur, they will be called a thioether, thioanisole, and thiophenol instead of ether, anisole, and phenol, respectively. In case where the thiol group is a substituent, the prefix mercapto- is used. When oxygen in the furan is replaced by the sulfur, it is called as thiophene.

the numbering in thiophene starts at the heteroatom and continues around the ring. In the same manner, benzofuran and dibenzofuran is named as benzothiophene and dibenzothiophene. But, like thiophene, the numbering in the dibenzothiophene does not start at the heteroatom. It starts as it is shown below, where substituents on the sulfur are numbered 5 instead of 1.

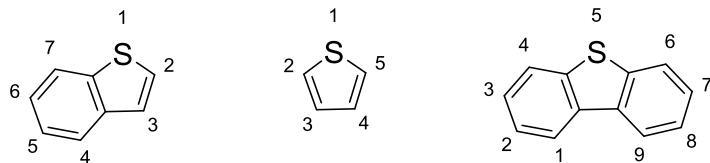


Figure 1. Structure of thiophene moieties.

An ylide is a neutral compound containing adjacent formal charges, generally negative on carbon and positive on heteroatoms like sulfur, phosphorus, or nitrogen. The names of the sulfonium ylides in Chapter 2 will be represented by placing the groups bonded to the anionic carbon, followed by the thiophene moiety and finally S,C-ylide. By convention, we also abbreviated dibenzothiophene as DBT, and then use that as a basis for other names. Thus DBTY is an ylide of DBT, but the specific formal name we use is dicarbomethoxy thiophene-S,C-ylide. The same pattern is used to name DCTY (Dicarbomethoxy-2,5-dichlorothiophene-S, C-ylide), where we are using DCT as an abbreviation for 2,5-dichlorothiophene.

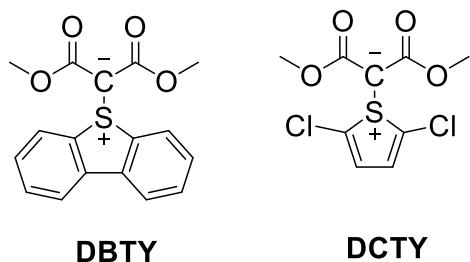


Figure 2. Structure of thiophene-S,C-ylides.

1.3 Photochemistry of thiophene-S,C-ylides

Thiophene-S,C-ylides generate a carbene intermediate on photolysis.²⁻⁴ The carbene is a six electron carbon species and has remained an important and interesting reactive intermediates in organic chemistry for various reasons, like the access they provide to unusual products, their differing chemistry based on the spin multiplicity, and mechanistic complexity. The two other major photochemical precursors to the carbenes are diazo compounds and diazirines. But these precursors will undergo reactions in their excited states⁵ that is exactly like the reaction of the carbene. So, the thiophene-S,C-ylides shown below were prepared and studied as an alternative precursors. An additional benefit of this strategy is that the chromophore is in the photochemical leaving group, which does allow for tuning of absorption and initial spin multiplicity distribution. The reactivity of the carbene depends on its spin multiplicity. Free singlet and triplet carbenes are highly reactive intermediates that have complementary reactivities. In understanding the reactions of carbenes, it is best to consider singlet carbene as a zwitterion and triplet as a diradical.

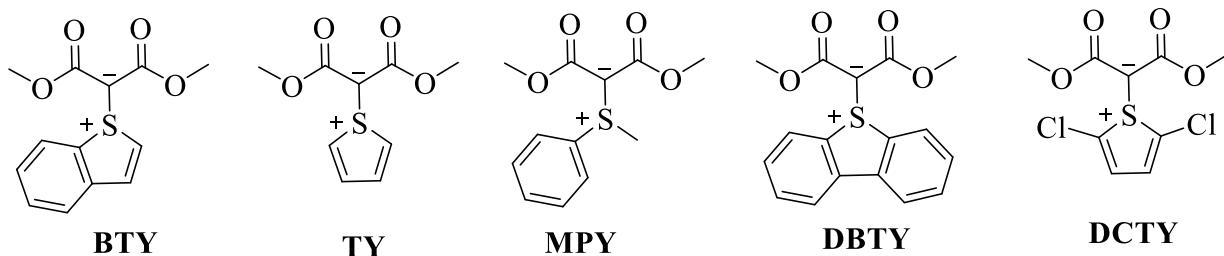


Figure 3. Structure of thiophene-S,C-ylides with varying thiophene moieties.

1.4 Reaction of carbene with methanol

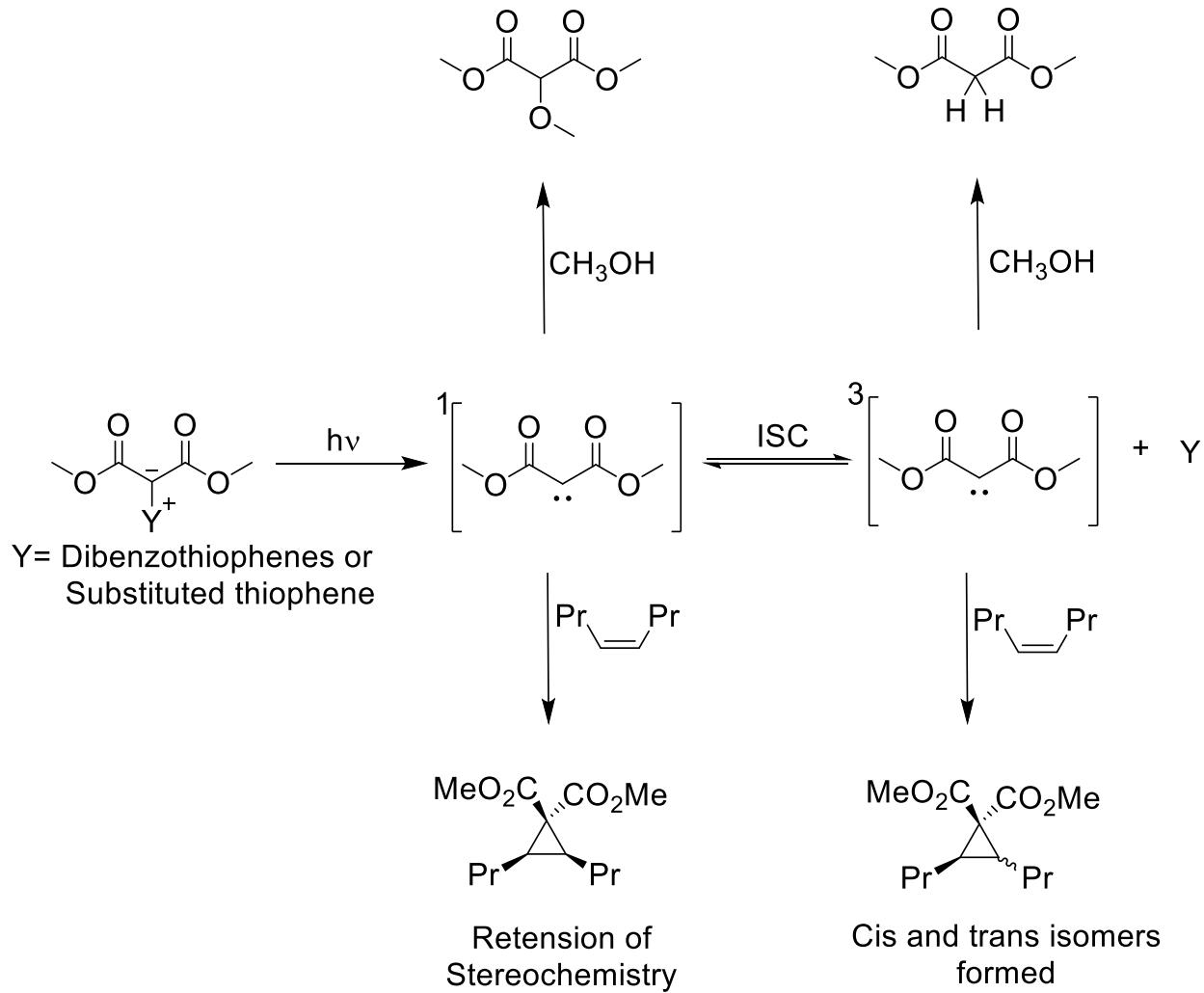
Singlet carbenes react at or near the diffusion-controlled limit with nucleophiles like methanol, undergoing a net insertion into the O-H bond of the alcohol via the formation of ylide intermediate. It was reported that the rate of the reaction of the singlet carbene in neat methanol⁵

is 10^{10} s⁻¹. The rate of intersystem crossing (ISC) from singlet to triplet carbene is not known. However, the observation of “singlet products” and “triplet products” depending on photolysis conditions shows that ISC in either direction is slow relative to the respective trapping rates. Triplet carbenes act as biradicals and undergo double hydrogen abstraction reactions in methanol. The rate of reaction of the triplet is likely to be 3 orders of magnitude slower than the singlet chemistry, based on other known rate constants.² Photolysis of the ylides in methanol resulted in different ratios of OH insertion product (dimethyl methoxy-malonate) and double hydrogen abstraction product (dimethyl malonate).

Another important aspect here regarding the singlet to triplet ratios is, most of the ylides have constant ratios with conversion, except the “parent” DBTY. In DBTY photolysis, the product ratios were conversion dependent. It was also reported that the initial spin distribution generated on the photolysis of the ylide can be strongly influenced by manipulating the thiophene portion of the ylide (different modifications were tried in altering the thiophene moiety like introducing heavy atoms like bromide, iodide, substituting selenium instead of sulfur to induce heavy atom effect). In chapter 2, we show that this conversion dependence is a result of the accumulation of DBT in the reaction mixture, which we show to act as a triplet sensitizer.

1.5 Reaction of carbene with alkene

Singlet carbenes react with alkenes in a concerted and stereospecific manner to form cyclopropanes with the complete retention of stereochemistry. Direct photolysis of diazomalonate was reported to give cyclopropanes with 90% retention of stereochemistry with cis-4-methyl-2-pentene.⁶ The 10% loss of stereochemistry was due to the reaction between the excited diazo compound and the alkene at high concentration bypassing the carbene completely. No evidence has been obtained for the sulfonium ylides doing excited state chemistry other than



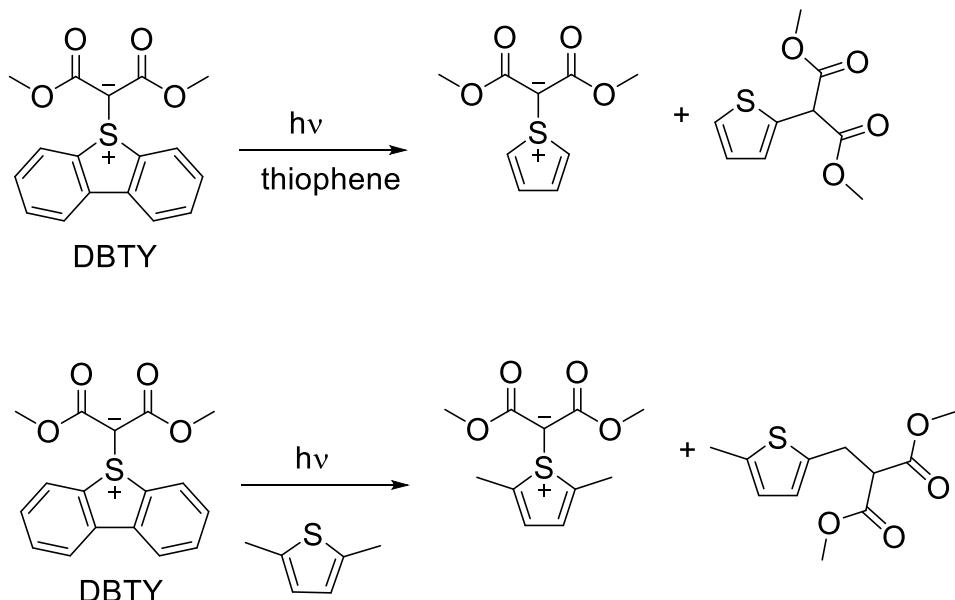
Scheme 1. Photolysis of thiophene-S,C-ylides in methanol and 10% Cis-4-octene.

leading to carbene formation.⁴ Thermolysis of the ylides was performed in 10% cis-4-octene as a control for 100% singlet activity with the generation of cis-cyclopropane with good mass balance.

Triplet carbene adds to olefins via stepwise radical addition to the double bond. A mixture of cis- and trans-products is generally observed because spin-flip of the intermediate biradical is slower than C-C bond rotation. So, the reaction of the carbene with cis alkene and the appearance of the trans cyclopropane is the evidence of the formation of triplet carbene.

1.6 Reaction of carbene with neat thiophene

When DBTY was photolyzed in neat thiophene two products were observed.³ One results from direct reaction between the sulfur atom of the thiophene with the carbene, i.e., making the new thiophene ylide. A second product is observed, in which a net insertion into the C-H bond at the 2-position of thiophene has occurred. Direct photolysis of DBTY using broad irradiation



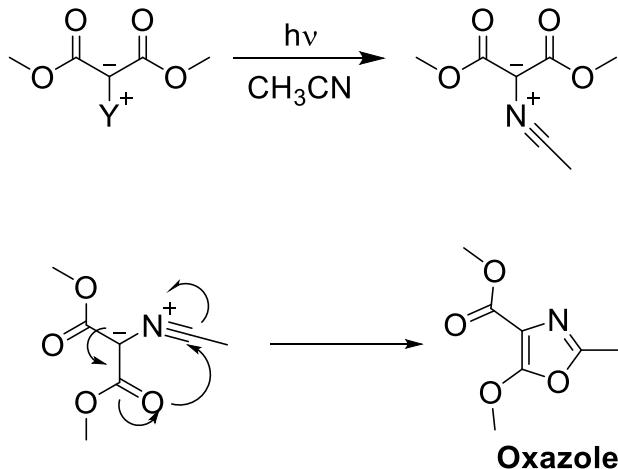
Scheme 2. Photolysis of DBTY in neat thiophene.

centered at 350 nm in neat thiophene formed (2-thienyl) malonate in nearly quantitative yields. When the 2 and 5 positions of the thiophene were substituted with bromides, chlorides, iodides, etc., only the analogs of ylide were observed and the product (2-thienyl) malonate was not observed. When 2,5 positions of the thiophene are methyl groups, in addition to the ylide, the product of the benzyl insertion was observed.³

1.7 Reaction of carbene with acetonitrile

An oxazole product was identified as the third product in addition to the cis and trans cyclopropanes in the photolysis of DBTY in 10% cis-4-octene in acetonitrile. Based on the data

of the direct and sensitized photolysis, oxazole was assigned to the product of the singlet carbene and the acetonitrile solvent.⁷ The proposed mechanism of the formation of the oxazole from the singlet carbene is as shown below.



Scheme 3. Mechanism of formation of oxazole from dicarbomethoxy carbene.

1.8 Nomenclature of dibenzothiophenium salts

When the sulfur atom of the thiophene or the sulfide is oxidized, the name of that oxidized sulfur compound depends on the number of oxygen atoms bonded to that sulfur atom. If the sulfur is bonded to one oxygen, it is called a sulfoxide and nomenclature uses that term or S-oxide, depending on formality. Thus, thiophene sulfoxide and thiophene-S-oxide are synonymous. It is called a sulfone if the sulfur is bonded to two oxygens, with nomenclature accepting, for example, thiophene sulfone or thiophene-S, S-dioxide. In chapter 2, we used dibenzothiophene-S-oxide (DBTO) as a nucleophile to alkylate the oxygen via an SN2 with an alkyl bromide or alkyl iodide. This forms S-alkoxy dibenzothiophenium salts⁸ as shown below (1a, 1b).

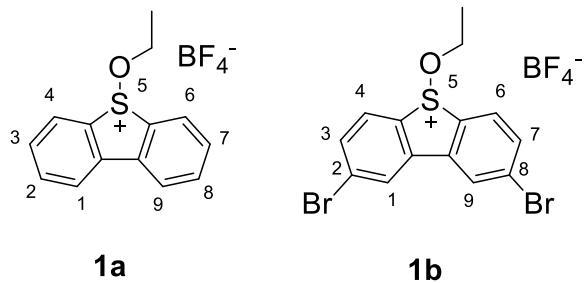


Figure 4. Structure of S-Ethoxy dibenzothiophenium and S-Ethoxy dibromodibenzothiophenium salts.

These compounds are salts, rather than ylides. Thus, we call **1a** S-ethoxy dibenzothiophenium tetrafluoroborate and **1b** is named as S-ethoxy-2,8-dibromodibenzothiophenium tetrafluoroborate.

1.9 Nomenclature of the pyridine precursors

The naming of the pyridinium precursors follows the same convention. Common names are used to name the aromatic and heterocyclic amines such as pyridine, pyrimidine, and 2-bromopyridine, and the accepted numbering schemes for those rings are observed. Like the thiophene derivatives, the pyridines can also be oxidized to its corresponding oxides.⁹⁻¹⁰ The oxidized pyridines get the positive charge on the nitrogen atom and the name of the oxidized pyridines ends with the suffix -N-oxide as in pyridine-N-oxide and 2-bromopyridine-N-oxide.

Pyridine-N-oxides are nucleophilic enough to act as a nucleophile to react with the alkyl bromide or iodide to form N-alkoxy-pyridinium perchlorates as shown below.¹¹ The salts were named starting with the alkoxy part attached to the nitrogen (as N-alkoxy), followed by the pyridinium perchlorate as in N-ethoxy pyridinium perchlorate (3a).

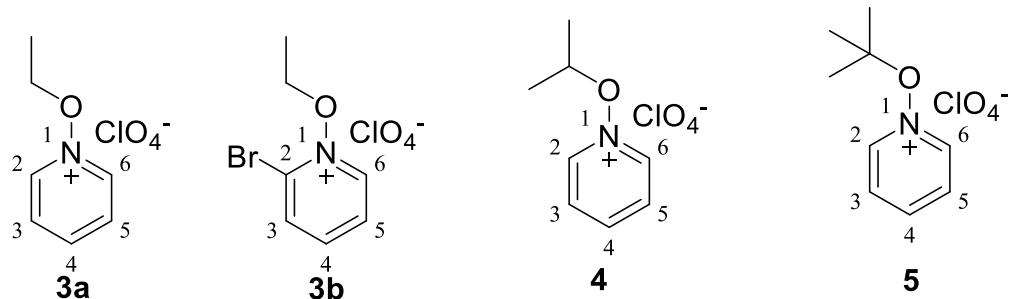


Figure 5. Structure of N-Alkoxy pyridinium perchlorate salts.

1.10 Photochemistry of N-Alkoxy pyridinium salts

Pyridinium salts such as N-alkoxy pyridinium and N-alkoxy quinolinium salts are reported to be capable of acting as photo-initiators for the cationic polymerization reaction of cyclic ethers such as cyclohexene oxide and vinyl ethers such as n-butyl vinyl ether.¹²⁻¹⁴ These salts are characterized by absorption maximums near 235, 270, and 300 nm. Some of the pyridinium, quinolinium, and isoquinolinium hexafluoro salts that are reported in the literature are shown below.¹³ These salts, on UV-irradiation, generate alkoxy radical and the corresponding radical cation of the leaving group (pyridine, 2-methylpyridine, and isoquinoline).^{13, 15}

On the other hand, All the thiophene sulfonium precursors that had been reported for the reactive intermediates (such as carbene, oxygen atom, nitrene)^{1-4, 16-19} undergo photo-heterolysis to generate the corresponding reactive intermediate and the neutral thiophene moiety as the leaving group. Sulfonium salts are reported to be one of the effective photo-initiators for the cationic polymerization reactions.²⁰ To the best of our knowledge, there are no reports of *S*-Alkoxy thiophenium salts being a photochemical precursors of alkoxy radical intermediate.

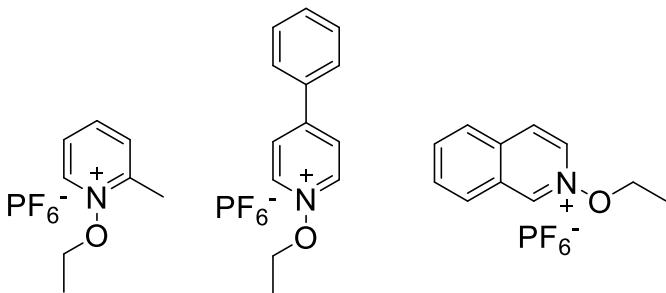


Figure 6. Structure of pyridinium and isoquinolium salts.

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CHAPTER 2. PRODUCT SENSITIZATION IN THE PHOTOCHEMICAL GENERATION OF CARBENES FROM SULFONIUM YLIDES

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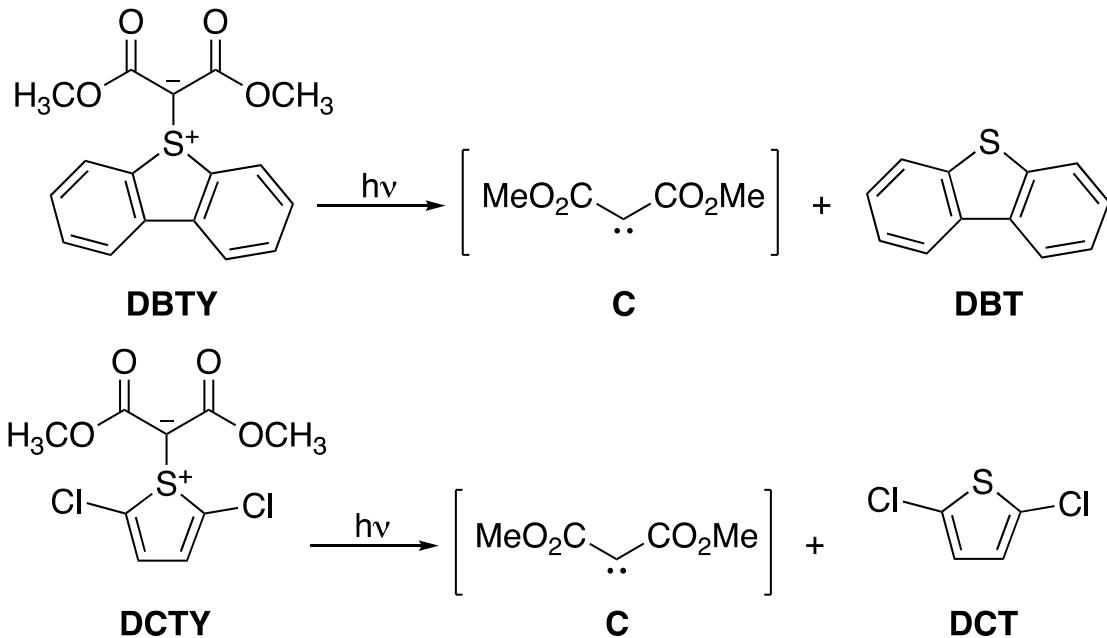
2.1 Abstract

Photolysis of thiophene ylides provides a route to certain carbenes with adjustable photophysical parameters, in that the absorption spectrum of the precursor and the initial spin population of the carbene can be varied. However, the accumulated thiophene from extensive photolysis can act as a triplet sensitizer leading to triplet carbene. It is demonstrated that dibenzothiophene has this property and 2,5-dichlorothiophene does not.

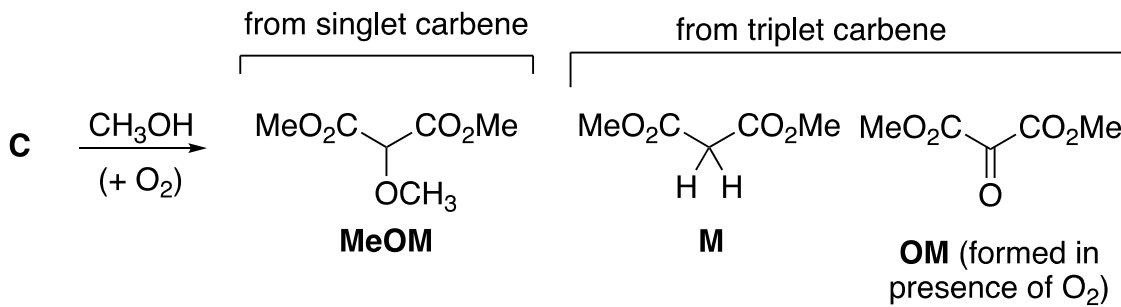
2.2 Introduction

S,C-Sulfonium ylides based on the thiophene moiety can be useful photochemical precursors of carbenes, as previously demonstrated for dicarbomethoxycarbene.¹⁻³ The reaction finds a good analogy to the formation of nitrenes from sulfilimines⁴⁻⁸ and atomic O(³P) from sulfoxides.⁹⁻¹⁸ As illustrated in Scheme 1, photolysis of ylides analogous to the dibenzothiophene ylide **DBTY** regenerates the aromatic sulfide (in this case dibenzothiophene, **DBT**), along with the transient carbene **C** (quantum yield ~0.16 for **DBTY**). Previous work demonstrated the important finding that the initial spin multiplicity distribution of the carbene depended on the exact nature of the thiophene derivative,^{1,3} thus allowing manipulation of that parameter. This phenomenon was attributed to the variation of photo-physics contained within the thiophene

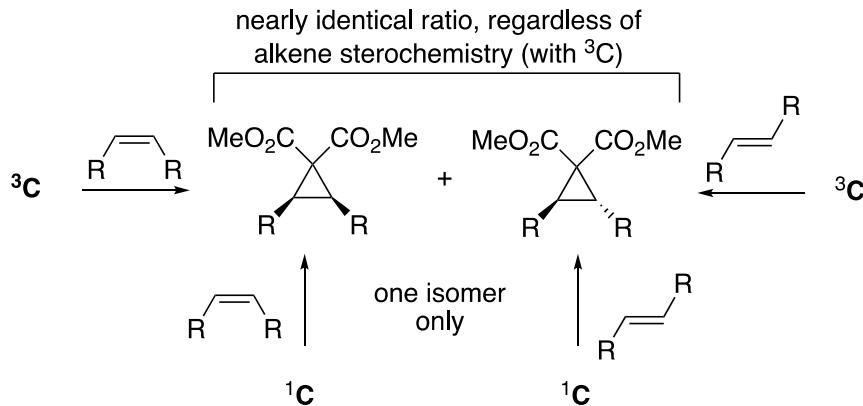
chromophores, as contrasted to the fixed photo-physics available from diazo compounds, where the chromophore of the photochemical leaving group cannot be varied. It is this latter feature of the thiophene ylides as a class (whether generating carbenes, nitrenes, or O(³P)) that can be exploited to make them attractive photochemical precursors for various reactive intermediates.



Scheme 1. Photochemical formation of dicarbomethoxy carbene, C.



Scheme 2. Reaction of dicarbomethoxy carbene with methanol.



Scheme 3. Reaction of dicarbomethoxy carbene with *cis* or *trans* alkenes.

Proof of this concept can be developed through trapping reactions that occur rapidly compared to the intersystem crossing of the carbene. Singlet dicarbomethoxy carbene (¹C) in neat methanol is trapped as methoxymalonate **MeOM**, whereas the triplet carbene (³C) is indirectly observed as the reduced malonic ester **M**. Adventitious or intentionally added oxygen diverts ³C to the oxomalonate **OM** (Scheme 2). Similarly, the addition of ¹C to alkenes to form cyclopropanes is stereospecific. A mixture of *cis* and *trans* cyclopropanes that favors the more stable isomer is obtained from either the *cis* or *trans* oct-4-ene and ³C (Scheme 3).

In our initial work,¹ we stated that control photolysis showed constant product ratios (e.g., **M**:**MeOM**) with conversion, but as shown here, that is not true in every case. This paper tests the hypothesis that the variation of such product ratios is due to triplet sensitization by the resulting sulfide product (e.g., **DBT**) in appropriate cases.

2.3 Results and Discussion

In the course of expanding work on this set of carbene precursors, a set of data was obtained for the direct photolysis of dibenzothiophene ylide (**DBTY**) at 270 nm in methanol showed that the product ratio obtained between methoxymalonate **MeOM** (the singlet-attributed product) and malonate **M** (the triplet-attributed product) was not constant with conversion

(Figure 1), in contrast to our prior generalization. In fact, extrapolation to zero conversion suggested that the initial product distribution was roughly 15% triplet-derived and 85% singlet-derived (hereafter noted as T:S = 15:85). It should be noted that detection limits made determining the product ratios at very low conversion untenable, so these initial product ratios are extrapolated and should be treated as qualitative data. (See supporting information for figures illustrating the same phenomenon in the remaining examples.)

Over the course of bringing the reaction to full conversion in just over 200 minutes, that ratio reversed smoothly to 68:32 (Table 1, entry 1). We use T:S₀ to denote the extrapolated product ratio at zero conversion and T:S_f to denote the observed final product ratio. As described below, similar time-course measurements were made for a series of related photolysis conditions. For example, photolysis with 300 nm excitation provided very similar results. See Table 1, entry 3.

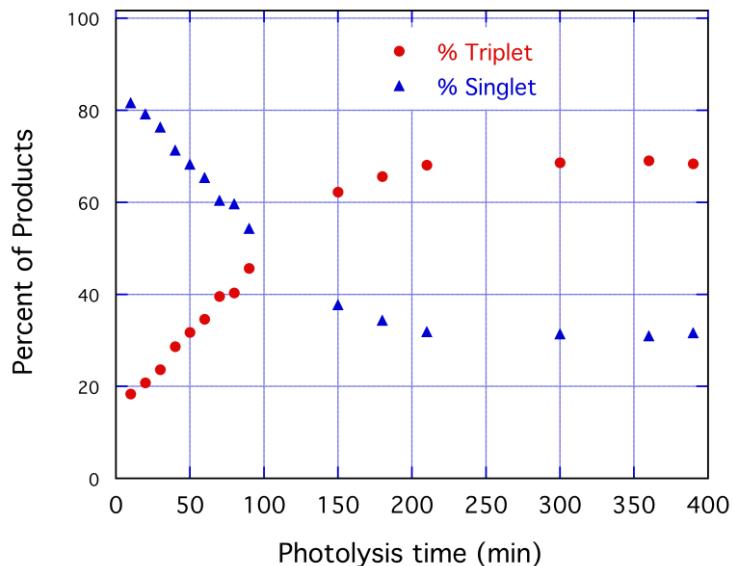


Figure 1. Product mixture for direct photolysis of **DBTY** at 270 nm as a function of photolysis time. The singlet product is **MeOM** and the triplet products are **M** and **OM**. Total yield at complete conversion is 72% for the three compounds, determined by comparison to formed **DBT**.

It was found that over the course of many septum piercings in some experiments, admission of adventitious oxygen meant that oxomalonate **OM** was formed in addition to **M**. Control experiments sampling only at the final time point showed that (**M + OM**) was approximately constant when only adventitious O₂ was present. Thus, both are counted as part of the triplet product mixture.

In retrospect, it was hypothesized from data in Figure 1 that the great difference between T:S_o and T:S_f was due to competitive absorption of light by accumulating **DBT**, which could be acting as a triplet sensitizer. According to literature data,¹⁹⁻²⁰ the triplet yield of **DBT** at room temperature is nearly quantitative ($\Phi_T = 0.97$). Thus, as **DBT** begins to compete with **DBTY** for light absorption, a new triplet-only channel is opened. This is because photons absorbed by **DBT** give rise to ³**DBT**, which can, in turn, form ³**DBTY** by energy transfer.

Table 1. Photolysis of DBTY in methanol.

Entry	[DBT] _o , mM ^a	λ_{ex} , nm	Gas ^b	T:S _o	T:S _f	% Yield ^c
1	0	270	Ar	15:85	68:32	72
2	7 (15%) ^c	270	Ar		75:25	78
3	0	300	Ar	14:86 ^d	71:29	61
4	0	300	O ₂	0:100	47:53	55
5	8 (79%) ^c	325	Ar	75:25	84:16	84

^aEstimate of the initial percentage of excitation light absorbed by **DBT** given in parentheses;

^bSolutions saturated with Ar to remove O₂, except entry 3, which was saturated with O₂; ^cSummed yield of **M**, **MeOM**, and **OM**. All yields are quoted at completion, summing all stated products, relative to **DBT**.

Photolysis of **DBTY** with added **DBT** was conducted with both 270 nm and 325 nm excitation. **DBT** and **DBTY** have considerable overlap in their absorption spectra, but the relative absorption of **DBT** is maximized at the longer of these two wavelengths. The initial fraction of light absorption by **DBT** under the conditions used was estimated at 15% at 270 nm and at 79% 325 nm (Table 1, entries 2 and 5). The data clearly show that the fraction of triplet product is maximized at 325 nm, as would be predicted if **DBT** acts as a sensitizer.

Another set of conditions involved intentionally adding molecular oxygen to the system, which is expected to have multiple effects (Scheme 4). First, O₂ should remove ³**DBT** by standard quenching pathways; the same should be true for ³**DBTY**, assuming the latter was sufficiently long-lived. By removing precursors to ³C, the observed product mixture should show a higher fraction of singlet-derived products, and the observed rate of the reaction should slow (i.e., the apparent Φ will drop). Indeed, the time to complete conversion was longer by ~3.5 fold by switching from bubbling with Ar to bubbling with O₂. In the presence of O₂, the T:S₀ ratio for direct photolysis of **DBTY** does, in fact, extrapolate to approximately 0:100 (Table 1, entry 4). This strongly indicates that ³**DBTY** is a species with a reasonable (ns-μs) lifetime. (No products obviously due to ¹O₂ were observed, though it is likely that this reactive oxygen species is formed. In the hands of this laboratory, ¹O₂ has not been observed to oxidize dibenzothiophene to its sulfoxide or sulfone analogs.) The T:S_f is also more biased toward singlet products with O₂ than in its absence.

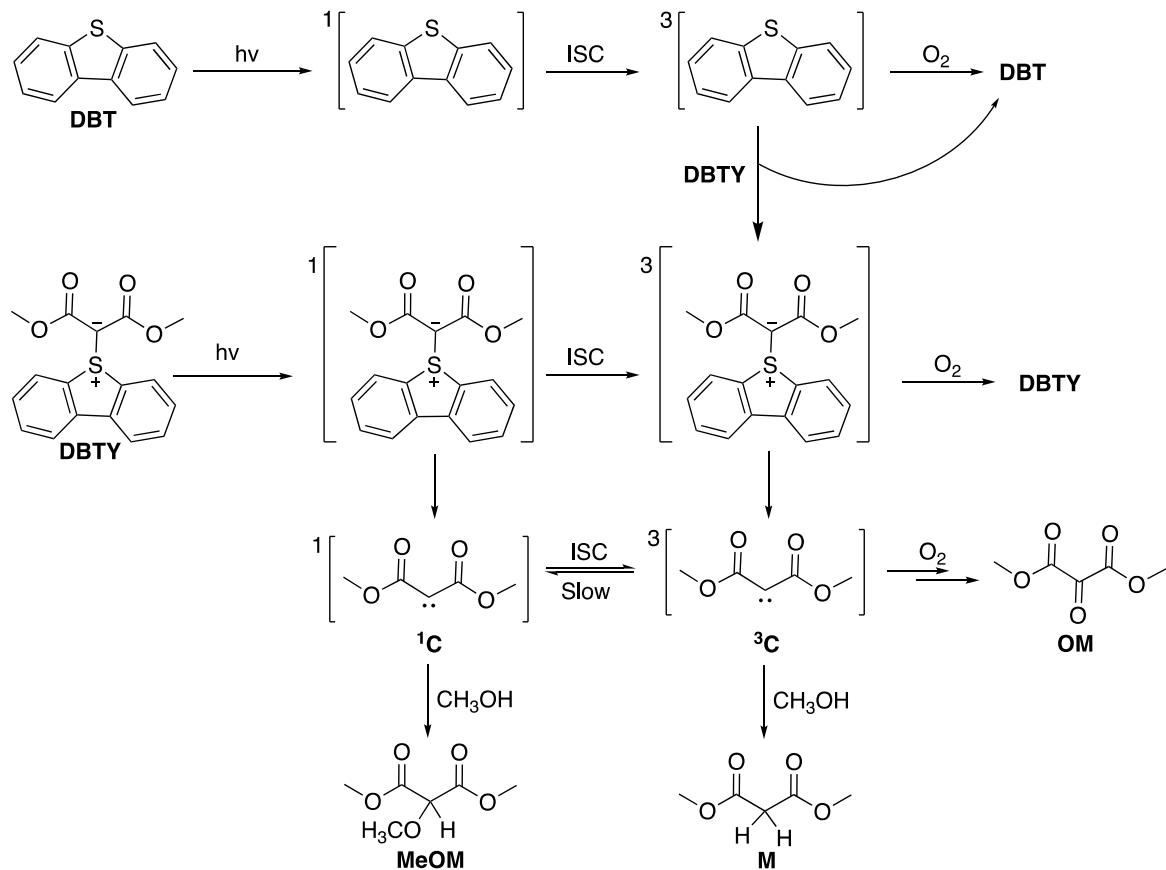
Photolysis of ylide **DBTY** was also carried out in a mixture of 10% (v/v) *cis* oct-4-ene in acetonitrile. The expected cyclopropanes are accompanied by the formation of oxazole **OZ**, which clearly derives from the coordination of the acetonitrile nitrogen with ¹C (Scheme 5). We further assume that ¹C produces the *cis* cyclopropane (**cCP**) stereospecifically, whereas the

triplet carbene produces a mixture of *cis* and *trans* cyclopropane, with the latter in predominance. Under these conditions, the expected carbene lifetime is only a few ns.²¹

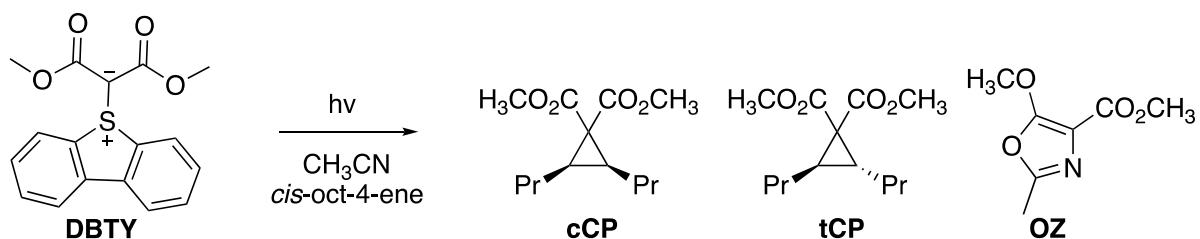
Direct photolysis of **DBTY** at 270 nm gave a product mixture at slight variance from our previous report,¹ with an initial *cis:trans* ratio that extrapolated to approximately 50:50, but was only 13:87 (Table 2, entry 1) at full conversion. The overall cyclopropane yield of 61% was accompanied by a 31% oxazole yield, making the overall mass balance quite good. It is not clear what precise changes in conditions account for the variation in ratio from our previous report, but we do note that the accumulation of sensitizer product does mean that the initial concentration will have an effect on the final mixture. The observed final product mixture should be sensitive to both excitation wavelength and initial concentration if the accumulated **DBT** byproduct acts as a sensitizer. A roughly 9:1 retention: inversion of stereochemistry was reported by Platz and coworkers on direct irradiation of diazomalonate in the presence of a related *cis*-alkene, with a roughly reversed ratio on benzophenone-sensitized photolysis.²¹

At the low conversion of **DBTY** on direct irradiation in acetonitrile, the major product is actually the oxazole **OZ**. This is consistent with it being the major product of the singlet carbene under these conditions. The time-course data confirm that oxazole formation slows dramatically (relative to the *trans* cyclopropane, in particular) in the latter third of the total conversion as the percentage of oxazole drifts down to its final value of 31%. (See figure 5 in supporting information.) This is in keeping with the notion that accumulating **DBT** competes for light absorption, and having done so, generates ³C by the triplet sensitization pathway. The current data set does not reveal the precise apparent *cis:trans* ratio for the addition of the triplet carbene to *cis*-oct-4-ene under these conditions. However, based on our previous and Platz's results, it should be roughly 10:90. Using this to estimate a "T:S_f" value as was done for photolysis in

methanol, the total triplet product must be in the range of 35%, in very reasonable agreement with the 32% estimate determined in methanol.



Scheme 4. Presumed kinetic scheme for photolysis of **DBTY** in methanol in the presence of O_2 . Oxygen is presumed to non-productively quench both ^3DBT and $^3\text{DBTY}$.



Scheme 5. Photolysis of **DBTY** in the presence of acetonitrile and cis-oct-4-ene.

In parallel, the methanol trapping data, photolysis of **DBTY** in octene/acetonitrile were also carried out in the presence of O₂. As expected, the percentage of singlet products increased and the reaction slowed considerably. However, the total mass balance drops to only 51% (Table 2, entry 2) (from 92% in the absence of O₂), so it is difficult to make quantitative arguments. Nonetheless, all trends are consistent with the data reported in Table 1, i.e., that O₂ quenches the triplet state intermediates. Experiments in octene/acetonitrile were also carried out with **DBT** added as a potential external sensitizer. Mass balance is estimated at 80%, and the total oxazole yield drops dramatically to 6% (Table 2, entry 3).

Table 2. Photolysis of DBTY in 10% Cis-4-octene in acetonitrile.

[DBT] ₀ , mM ^a	λ _{ex} , nm	Gas ^b	CP _f (%) ^c	CP cis:trans ₀	CP cis:trans _f	OZ _f (%)	T:S _f
0	270	Ar	61	50:50 ^d	13:87	31	66:34
0	270	O ₂	19		19:81	32	37:63
5 (96%)	323	Ar	74	21:79	14:86	6	91:9

^aEstimate of the initial percentage of excitation light absorbed by **DBT** given in parentheses;

^bSolutions saturated with Ar to remove O₂, or saturated with O₂; ^c Summed yield of **tCP**, **cCP**,

and **OZ**. All yields are quoted at completion, summing all stated products, relative to **DBT**;

^dGreater uncertainty than comparable zero-conversion data.

In order to further confirm this explanation of curved yield plots, sets of analogous data were collected for the photolysis of ylide **DCTY**, derived from 2,5-dichlorothiophene (**DCT**). We believed it to be a very reasonable expectation that dichlorothiophene would be a poor triplet sensitizer, being unaware of any precedent for its use for that purpose or for it having a long

Table 3. Photolysis of **DCTY** in methanol

[DBT] _o , mM ^a	λ_{ex} , nm	Gas ^b	T:S _o	T:S _f	Absolute yield (%) ^c
0	285	Ar	0:100	0:100	64
3 (60%)	285	Ar	70:30	70:30	65
3.5 (77%)	323	Ar	79:21	79:21	56

^aEstimate of the initial percentage of excitation light absorbed by **DBT** given in parentheses;

^bSolutions saturated with Ar to remove O; ^c Summed yield of **M**, **MeOM**, and **OM**. All yields are quoted at completion, summing all stated products, relative to **DCT**.

lived triplet state formed in high quantum yield (i.e., the ordinary conditions for being a good triplet sensitizer). If **DCT** does not form a long lived triplet, then the accumulation of **DCT** should not change the relative fraction of products throughout the photolysis, even if it does eventually compete with **DCTY** for light absorption.

As indicated in Table 3 (entry 1), photolysis of **DCTY** in methanol yielded no detectable triplet product (**M**), with **MeOM** formed in moderately good absolute yield. Self-evidently, **DCT** is unable to act as a triplet sensitizer for **DCTY**. However, a positive control is required, and thus photolysis of **DCTY** was repeated, using added **DBT**. Again, the expected result was obtained: a much higher contribution of triplet products (Table 3, entries 2 and 3), but at an essentially constant fraction throughout the course of the photolysis. Although the mass balance is not great in any of these photolysis, it is at least fairly constant, whether the photolysis is direct or sensitized.

Similarly, photolysis of **DCTY** were carried out in the same 10% *cis* oct-4-ene in acetonitrile mixture as for **DBTY**. Again, product proportions were invariant with the

Table 4. Photolysis of **DCTY** in 10% cis-oct-4-ene in acetonitrile:

[DBT] _o , mM ^a	λ_{ex} , nm	Absolute			Cyclopropane Cis:transf	Absolute Oxazole yield (%)	% Singlet
		Gas ^b	CP Yield (%) ^c				
0	290	Ar	6		83:17	90	99
5 (90%)	323	Ar	62		16:84	28	31

^aEstimate of the initial percentage of excitation light absorbed by **DBT** given in parentheses;^bSolutions saturated with Ar to remove O₂; ^cAll yields are quoted at completion, summing all stated products, relative to **DBT**.

conversion. Direct photolysis (Table 4 entry 1) provided only a very small fraction of triplet products, but photolysis in the presence of additional **DBT** provided considerably more triplet derived product mixtures (Table 4 entry 2).

2.4 Conclusion:

Sulfonium ylides such as **DBTY** and **DCTY** remain viable and important potential carbene precursors, where variations in the photophysics of the sulfur-bearing moiety will result in a difference in the initial spin distribution of the reactive intermediate. Additionally, the absorption window can be shifted. However, it is now also clear that when the thiophene derivative byproduct is allowed to accumulate in the reaction mixture, there is the potential for that compound to act as a triplet sensitizer and thus affect the obtained product distributions. In particular, it is demonstrated that **DBT** accumulation does effect triplet sensitization that affects reaction mixtures at an accumulation of a few mM, while **DCT** accumulation does not.

2.5 Experimental Section

General synthesis of compounds

The ylides **DBTY** and **DCTY** were prepared as described previously¹⁻³. The *cis*-cyclopropane **cCP** was isolated as a pure compound and the *trans* cyclopropane **tCP** was prepared as a mixture²². Commercially available oct-4-enes were distilled under Ar from CaH₂ to remove small quantities of oxidized impurities. Solvents were the highest grade commercially available. Methanol was used as received. Acetonitrile was ≤30 ppm water commercially and handled to minimize air exposure.

General method of photolysis

Photolysis was carried out much as previously described. Briefly, solutions containing the ylide were prepared in initial concentrations of 5-8 mM in the solvent of interest. Dodecane at 0.50 mM was used as an internal standard for GC analysis; a standard DB-5 (5% phenyl) microbore column was used for separation. Unless otherwise noted, solutions in methanol had no other initial components; photolysis using *cis*-oct-4-ene as the trap was done with 10% alkene in acetonitrile (v/v) instead of methanol. Solutions were deoxygenated or saturated with oxygen by bubbling for *ca.* 20 minutes with Ar or O₂, respectively. Sample volume was 3.0 mL in a standard 1 cm fluorescence cell equipped with a small stir bar and sealed with a septum for sparging and sampling through a needle. The light source was a 75 Xe lamp filtered through a monochromator set to ±12 nm dispersion. Samples were mounted directly in front of the monochromator exit slit and magnetically stirred to ensure even irradiation. GC retention times and relevant response factors were determined with authentic samples. Samples for GC injection (e.g., for watching the time course of a reaction) were obtained by piercing the septum with a GC needle and withdrawal a couple of microliters.

General extrapolation of plots

Extrapolations of product ratios to zero conversion were done by polynomial fits to appropriate fractions of the data sets. No physically meaningful inferences were made from fit data, but it was assumed that the curves would extrapolate smoothly. Thus, greater uncertainty should be attributed to product ratios at zero conversion than to those at full conversion, which were determined directly. For the photolysis in *cis*-oct-4-ene/acetonitrile mixtures, estimation of the total percentage of products derived from singlet or triplet carbene requires knowledge of the cyclopropane mixture hypothetically generated by a sample of pure ${}^3\text{C}$. Based on our previous work and a closely related reaction studied by Platz and coworkers,²¹ a 9:1 ratio of *trans* to *cis* was used for this study, and residual *cis* cyclopropane from observed ratios was attributed to singlet chemistry, as was observed oxazole.

2.6 Acknowledgments

The authors thank Iowa State University for support of this work.

Supplementary Data

Data analogous to Figure 1 for other experiments and UV data are available in the supplementary data.

Supplementary Data

Photolysis traces

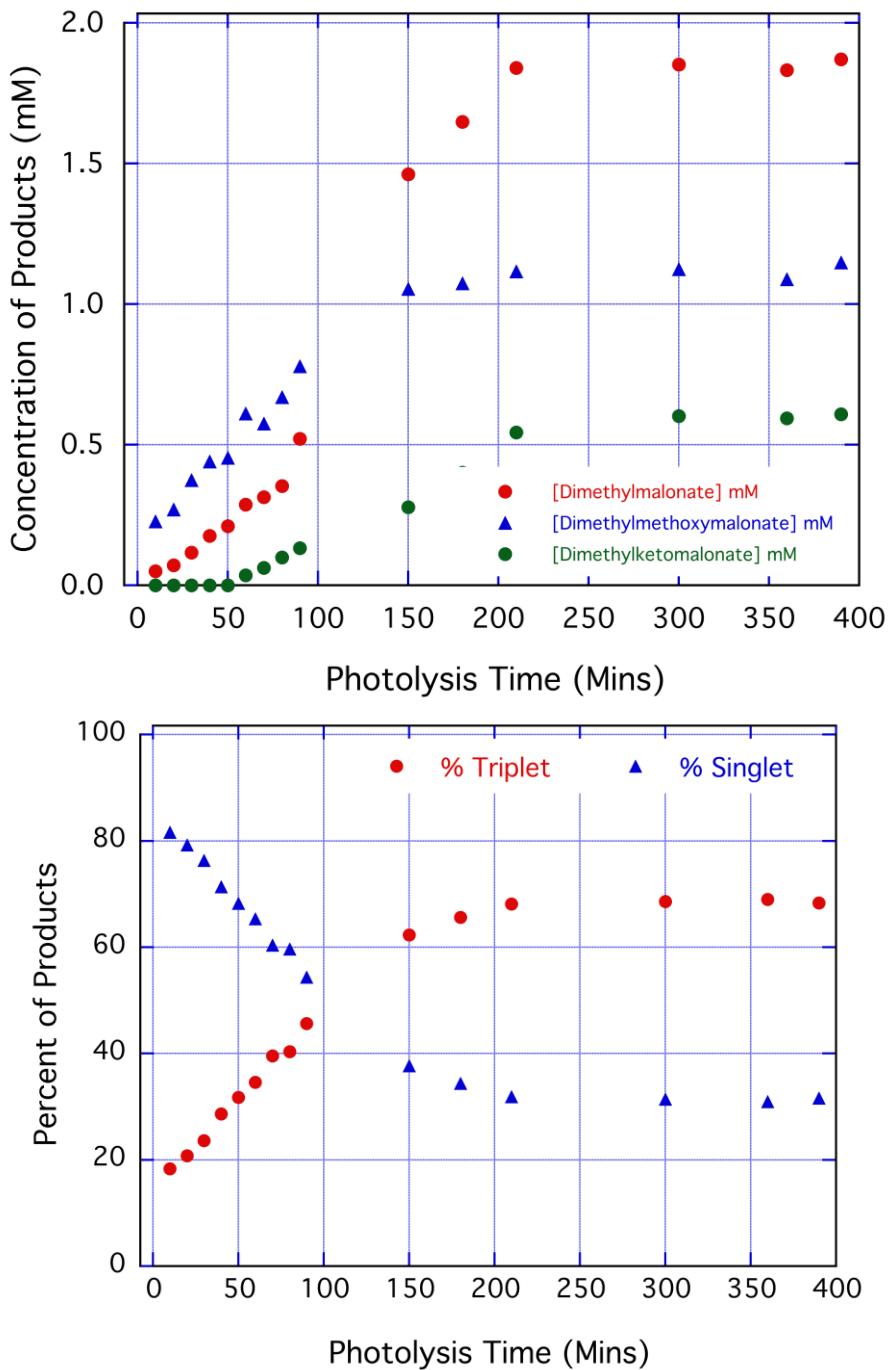


Figure S1. Direct photolysis of DBTY in methanol saturated with Ar at 270 nm.

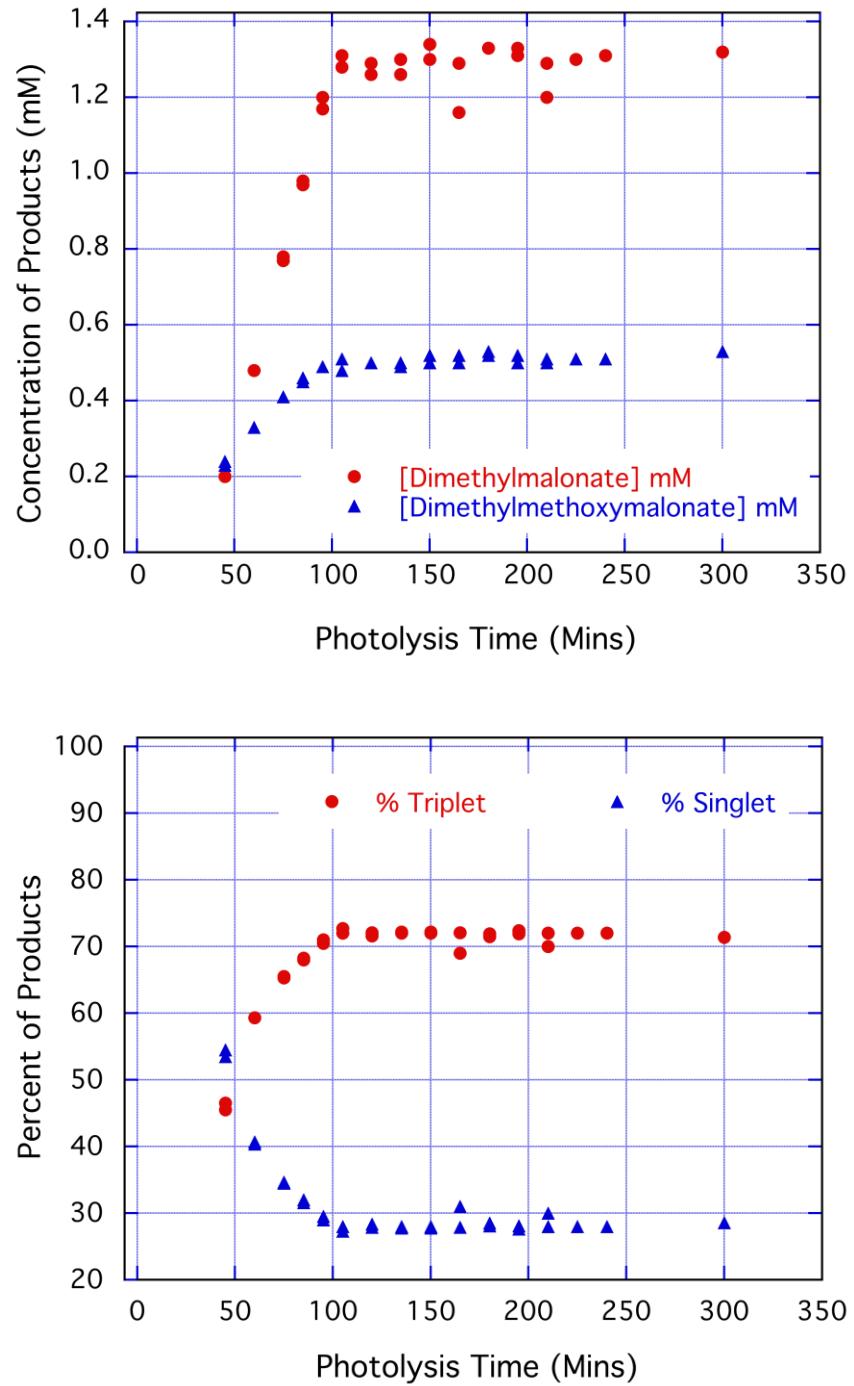


Figure S2. Direct photolysis of DBTY in methanol saturated with Ar at 300 nm.

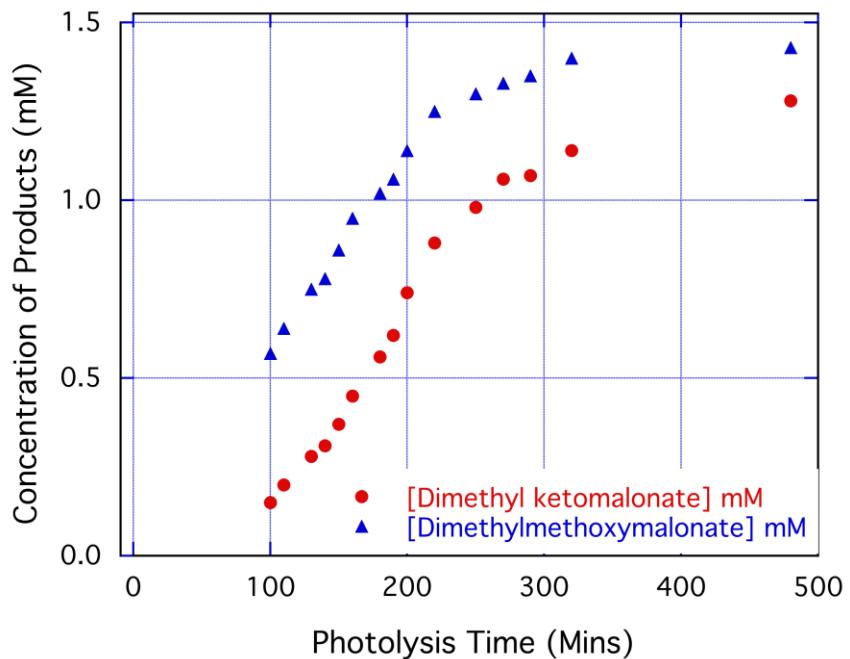


Figure S3. Direct photolysis of DBTY in methanol saturated with O₂ at 300 nm.

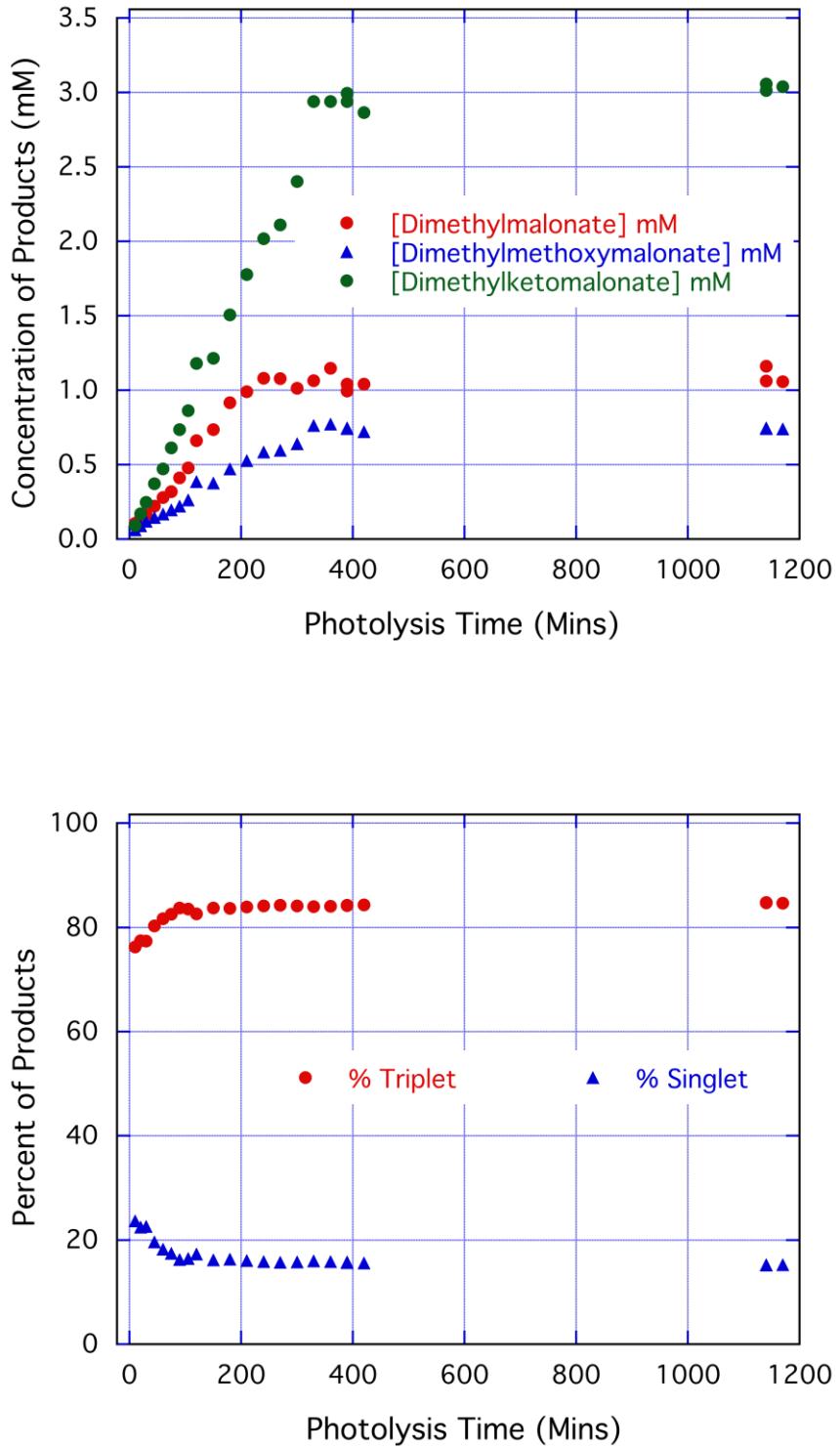


Figure S4. DBT sensitized Photolysis of DBTY in Methanol saturated with Ar at 325 nm.

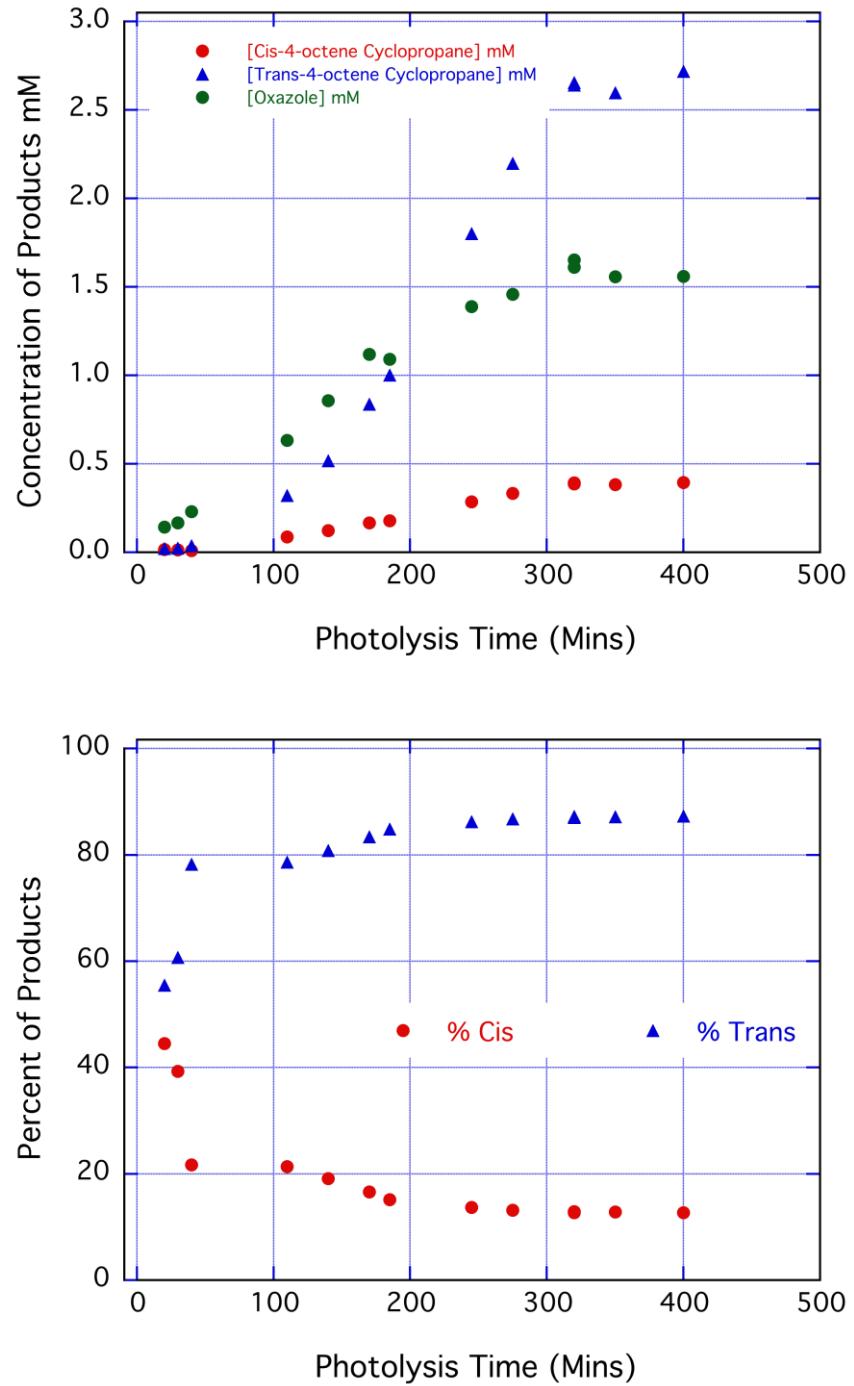


Figure S5. Direct photolysis of DBTY in 10% *cis*-4-octene saturated with Ar at 270 nm.

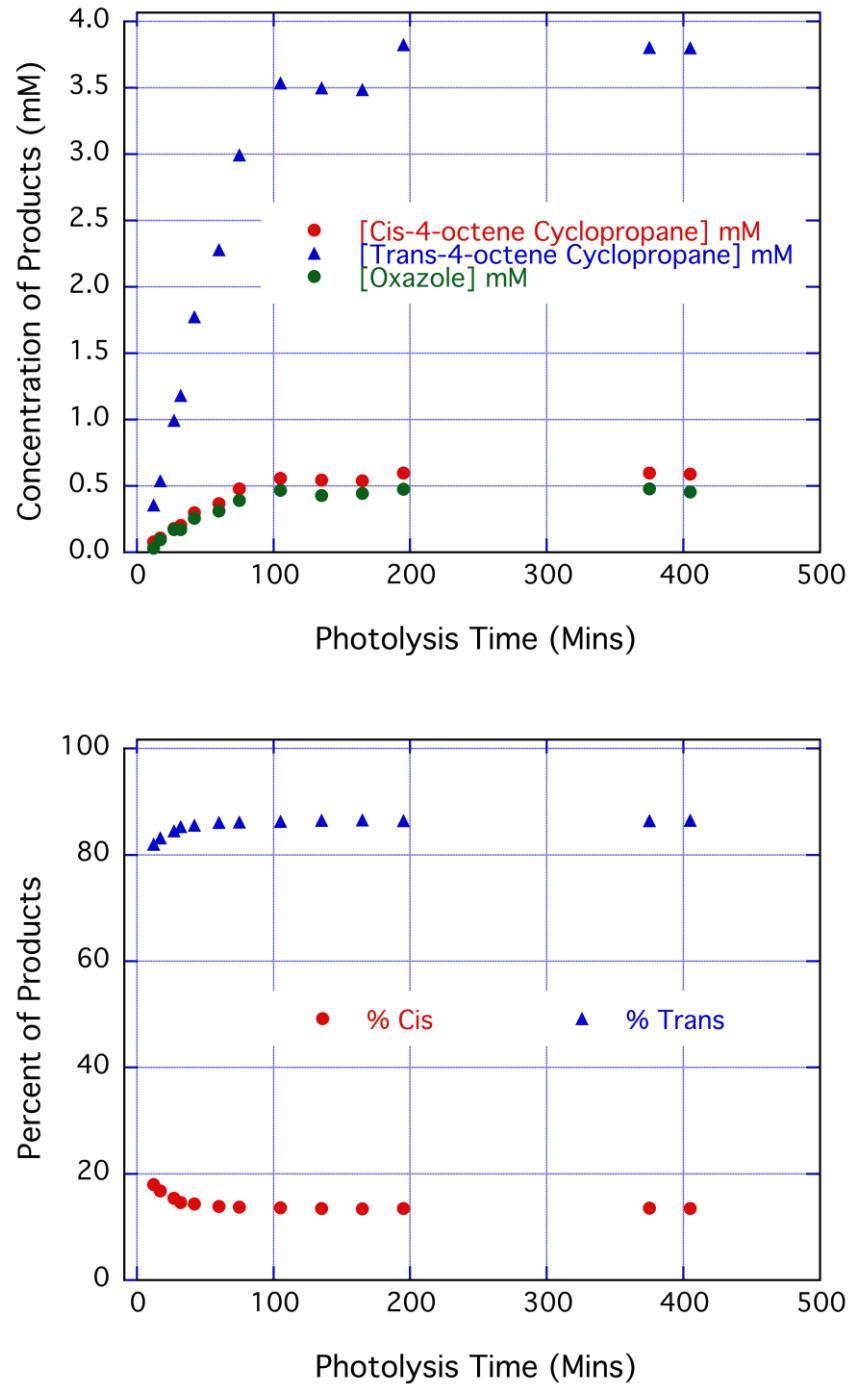


Figure S6. DBT sensitized Photolysis of DBTY in 10% Cis-oct-4-ene saturated with Ar at 323 nm.

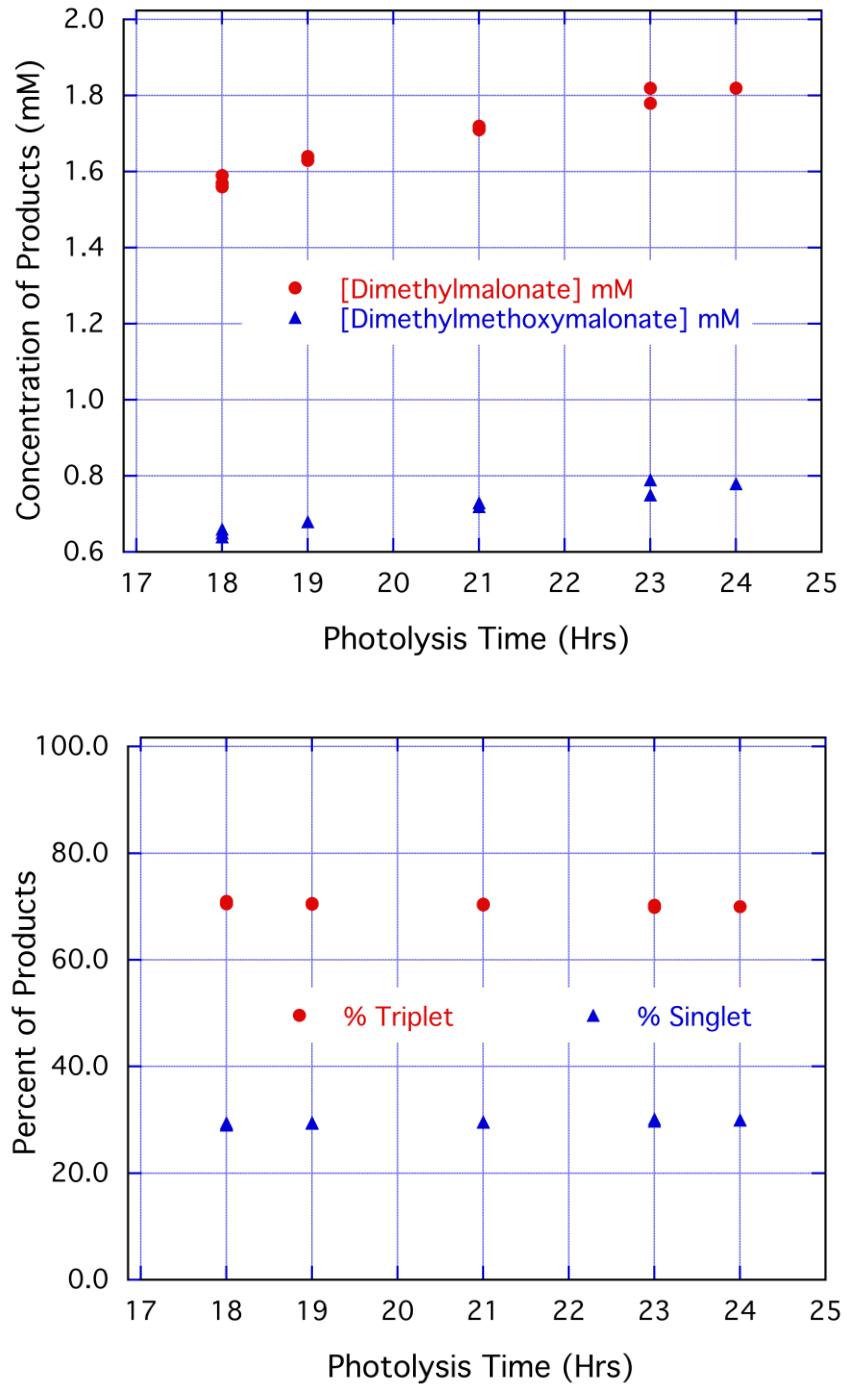


Figure S7. DBT sensitized Photolysis of DCTY in methanol saturated with Ar at 285 nm.

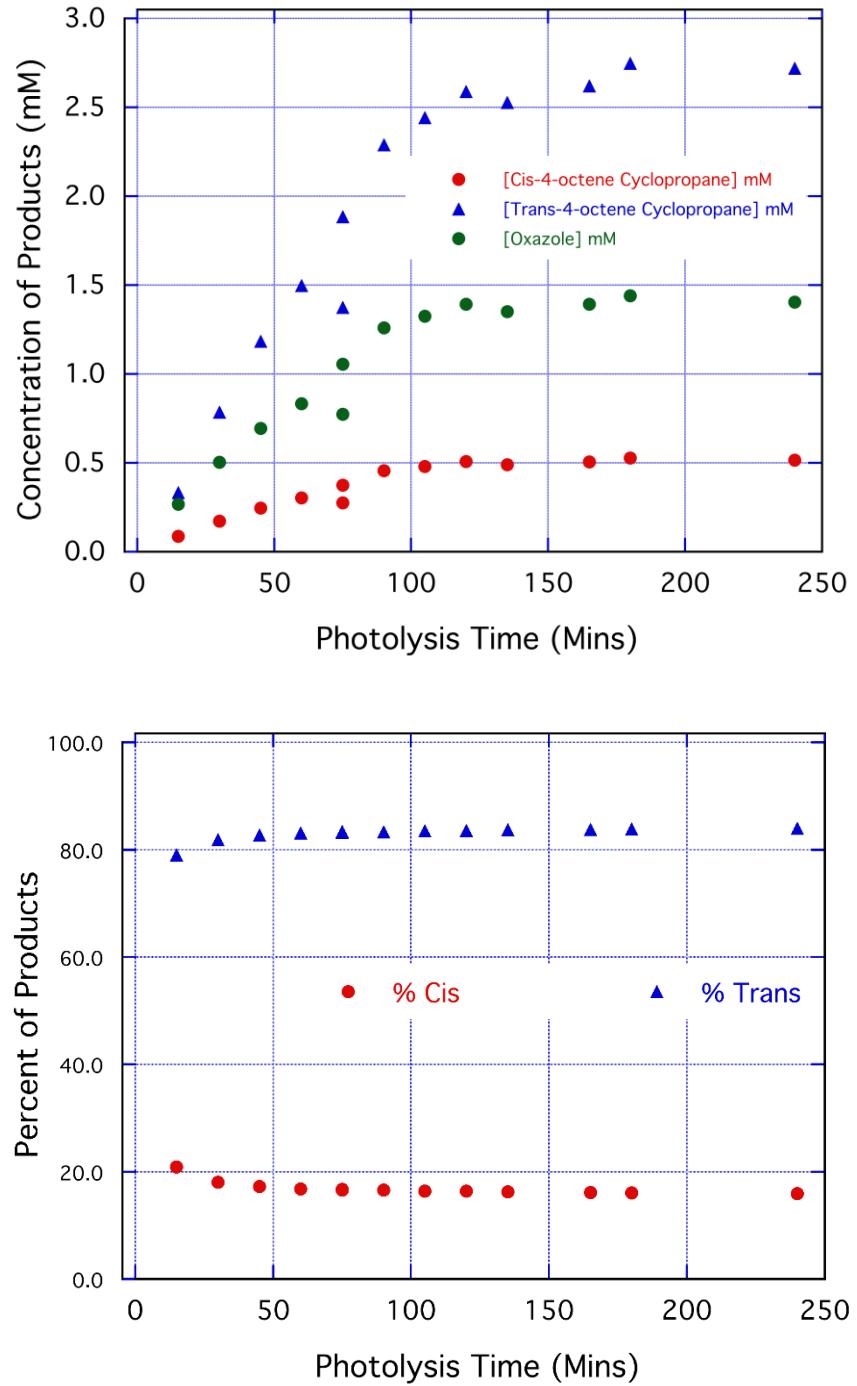


Figure S8. DBT sensitized Photolysis of DCTY in 10% *cis*-oct-4-ene saturated with Ar at 323 nm.

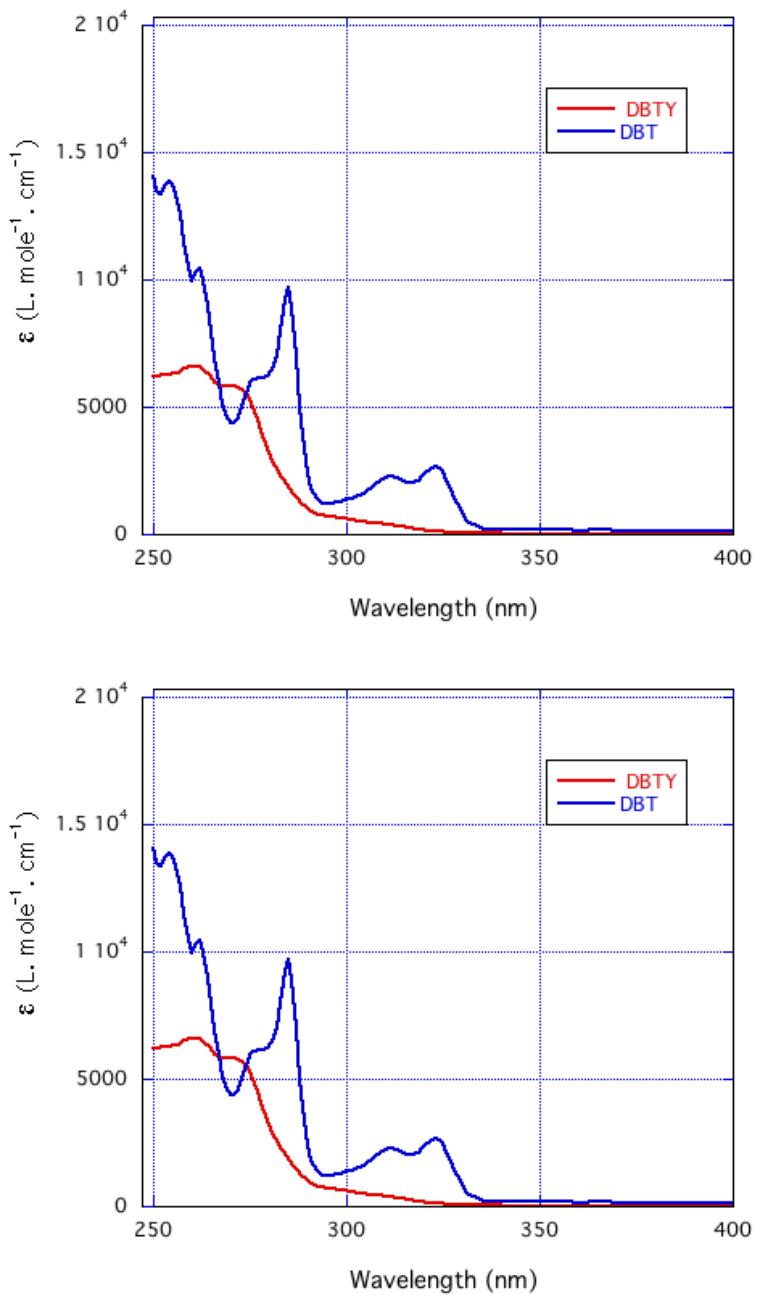
Quantitative UV-Vis Spectra

Figure S9. UV absorption spectra of DBT and DBTY in acetonitrile (top) and methanol (bottom).

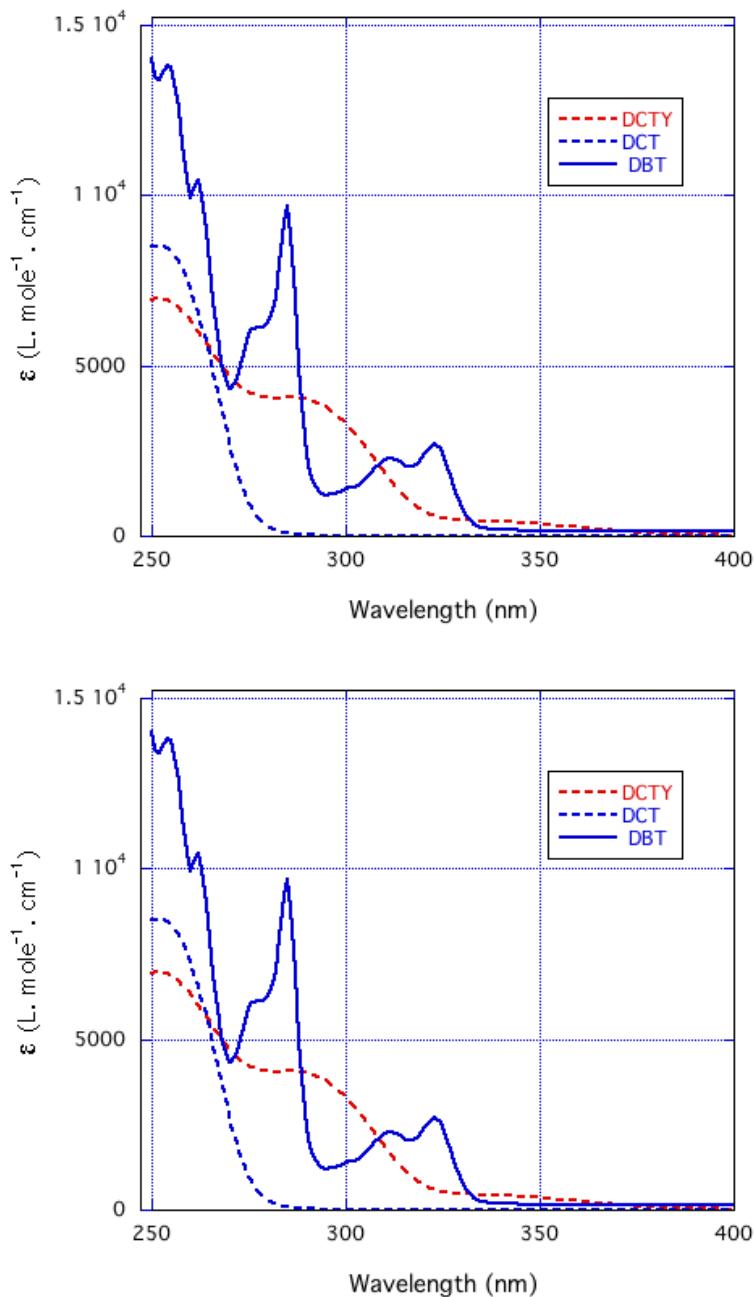


Figure S10. UV absorption spectra of DBT, DCT, and DCTY in acetonitrile (top) and methanol (bottom).

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CHAPTER 3. S-ALKOXY DIBENZOTHIOPHENIUM AND N-ALKOXY PYRIDINIUM SALTS: HETEROLYTIC vs HOMOLYTIC PHOTOCHEMICAL FRAGMENTATION

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Modified from an article that is going to be published in Organic Letters

3.1 Abstract

S-alkoxy dibenzothiophenium and N-alkoxy pyridinium salts are prepared and photolyzed to explore the potential homolytic and heterolytic paths of the photochemical S-O cleavage of the thiophenium salts. The heterolytic path would generate a highly unstable electron-deficient alkyl oxenium ion and the corresponding neutral leaving group. Homolysis would generate an alkoxy radical and the corresponding radical cation of the leaving group. The evidence obtained suggests the homolytic formation of alkoxy radical and radical cation of the leaving group though some fraction of the oxenium and the neutral leaving group cannot be ruled out completely.

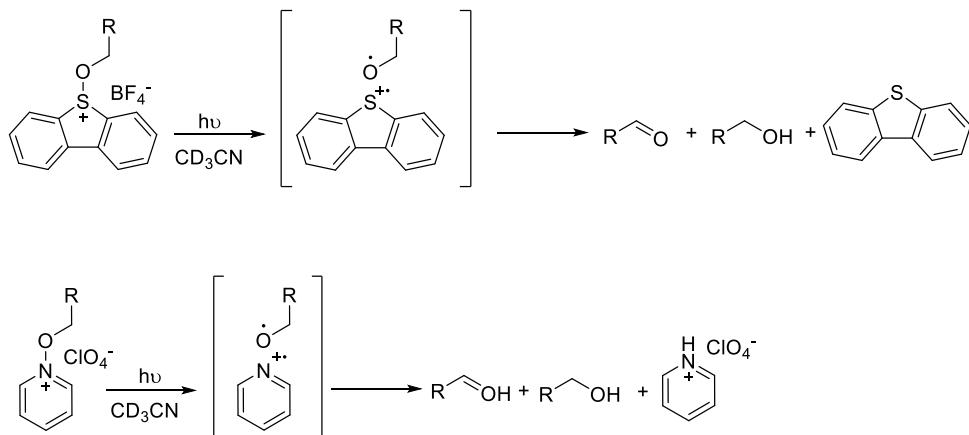


Figure 1. Photolysis of dibenzothiophenium and pyridinium salts in acetonitrile-d₃.

3.2 Introduction

Oxenium ions are highly reactive intermediates that have two pairs of non-bonding electrons and a formal positive charge on the highly electronegative oxygen atom — and they are thought to be highly electrophilic.¹⁻⁴ They are proposed as an intermediate in various synthetic transformations like electrochemical oxidation of phenols and phenolates for the generation of commercially useful polymers like poly 2,6-dimethyl-1,4-phenylene oxide⁵⁻⁹ and for super-acid catalyzed the oxidation of alkanes,¹⁰ Observational evidence for the existence of biphenyl oxenium ion as an intermediate came from transient absorption and kinetic studies of its formation and decomposition in aqueous solution by Novak and coworkers.^{7, 11-18} They report a lifetime of 170 ns for *p*-biphenyloxenium in water.¹² They used neutral precursors that undergo heterolysis to generate the ion pair but determined that photohomolysis is competitive, even in protic solvents.

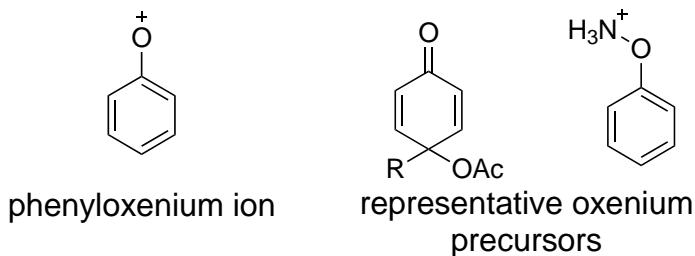


Figure 2. Structure of phenyloxenium ion and its respective precursors.

Winter and co-workers used DFT studies to determine that simple aryloxenium ions like phenyloxenium ions have closed-shell singlet ground states, though certain substitutions (e.g., *meta*-amino) could put the triplet in the ground state.¹ They reported the direct detection of closed-shell singlet phenyloxenium in three low-lying electronic states (closed-shell singlet, open-shell singlet, and triplet) ranging from the femtosecond to the microsecond time scale.¹⁻⁴

In recent years, it has been shown that dibenzothiophene (and related derivatives) serve as appropriate photochemical leaving groups for the formation of a variety of 6-electron intermediates, including oxygen atoms,¹⁹⁻²¹ carbenes,²²⁻²⁵ and nitrenes.²⁶⁻²⁷ We thus investigated whether sulfonium salts might analogously generate oxenium ions. An advantage here, in principle, was that simple alkyl oxenium ions could be generated since the chromophore is in the leaving group. This study was intended to lay the groundwork for a potentially more aggressive flash photolysis investigation that might be able to address such questions as to whether a singlet alkyl oxenium ion is even a thermodynamic minimum along the pathway that leads to a protonated aldehyde via hydride migration.

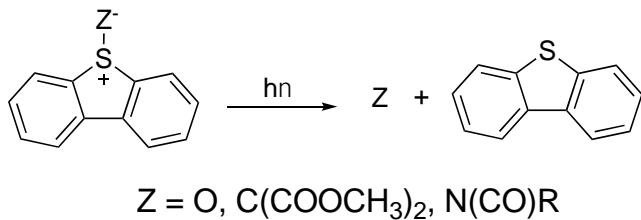
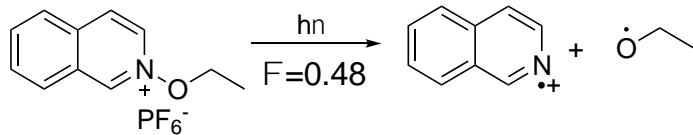


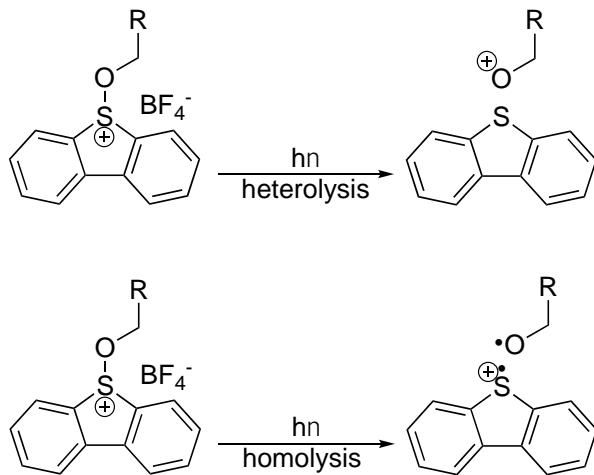
Figure 3. Representation of dibenzothiophenium ylide being the precursor of O-atom, Carbene and Nitrene.

At least potentially competing with the heterolytic photochemical cleavage to make the notoriously unstable oxenium ions, a homolytic S-O cleavage could occur, which would initially give rise to the sulfur-bearing radical cation and alkoxy radical, as shown in Scheme 1. A precedent for this pathway has not been seen in our previous investigation of the organosulfur compounds, but it is widely believed that photolysis of N-alkoxy derivatives of pyridine, quinoline, isoquinoline, and phenanthridine are photochemically cleaved in the homolytic mode, generating alkoxy radicals and nitrogen-based radical cations.²⁸⁻³³ A quantum yield of 0.48 for *N*-ethoxy quinolinium photohomolysis has been reported.²⁸ These compounds also rapidly and

efficiently produce alkoxy radicals on photochemical intramolecular electron transfer³² or intermolecular electron transfer.³⁴⁻³⁵



Scheme 1. Heterolytic vs. homolytic photocleavage of S-alkoxy dibenzothiophenium salts



Scheme 2. Potential paths of photolysis of dibenzothiophenium salts

A second interest in the thiophene ylide precursors is that previous studies have shown that the use of different thiophene derivatives as a basis for the ylide leads to different initial mixes of singlet and triplet spin multiplicity carbenes²²⁻²⁵ and nitrenes.²⁶⁻²⁷ This was accessible – at least qualitatively – through simple product study because these intermediates react rapidly with solvent, i.e., more quickly than they get to spin equilibrium; thus, for example, dicarbomethoxy carbene provides a different mix of dimethyl malonate (triplet product) and dimethyl methoxymalonate (singlet product) when produced by photolysis of various thiophene ylide derivatives in methanol.²²⁻²³ We postulated that a similar differentiation might be made

from oxenium ions, expecting aldehydes and alcohols for singlet and triplet species, respectively. Complicating this, of course, was the possibility that similar products might be observed from the homolytic pathway.

In this paper, we report the observation that indeed alcohols and aldehydes are observed on photolysis of S-alkoxy thiophenium derived cations. However, through modifications of the thiophenes with bromine as a heavy atom substituent, comparison to *N*-alkoxypyridinium precursors, and control experiments involving trapping by molecular oxygen, we show that the predominant pathway for the *S*-alkoxy thiophenium salts appears to be homolytic, rather than heterolytic.

3.3 Results and discussion

3.3.1 Compound selection and preparation

S-Alkoxy dibenzothiophenium tetrafluoroborate salts were prepared with a simple ethoxy group and a 3-phenylpropoxy group intended to make GC and/or NMR analysis of certain products easier. Each was prepared with and without bromine substitution on the dibenzothiophene (DBT) nucleus, the motivation being to provide at least a modest heavy atom effect on the formation of the reactive intermediates; that is, to potentially increase the initial yield of reactive intermediates born with triplet spin multiplicity. These were prepared by the method of Acheson³⁶ which consists of nucleophilic substitution on an alkyl iodide or bromide by the corresponding sulfoxide in the presence of Ag⁺ ions. Analogous secondary and tertiary alkoxy compounds could not be isolated, in agreement with previous reports of the instability of such materials.³⁷⁻³⁸

It was anticipated that if compounds **1** and **2** were to generate oxenium ions by heterolysis with singlet multiplicity, they would nearly instantaneously rearrange to protonated

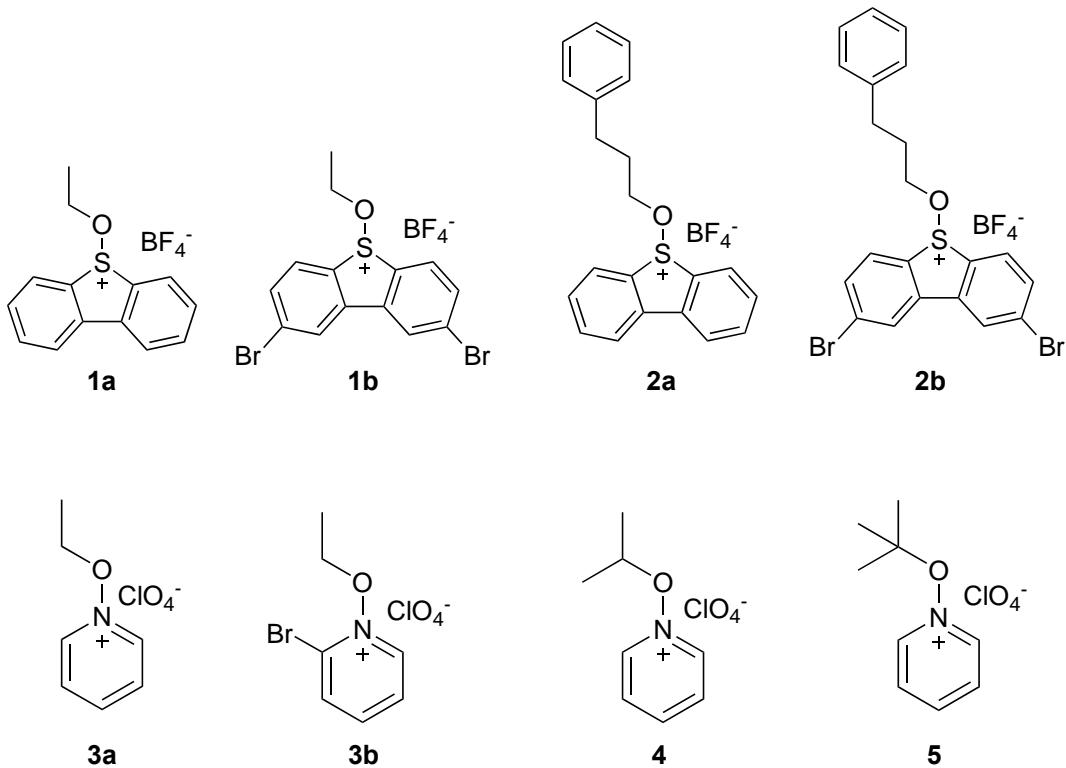
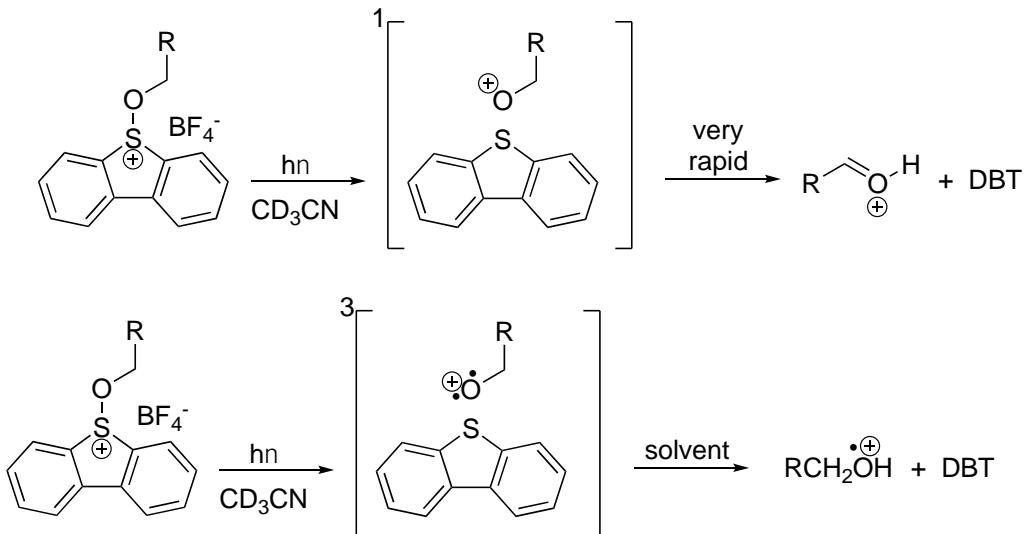


Figure 4. Dibenzothiophenium and pyridinium salts reported in this project.

aldehydes. (These are of course observed as the ordinary deprotonated aldehyde.) Although the triplet reactivity was not quite as clear to anticipate, it was thought that a very electrophilic oxygen centered “radical cation” would probably abstract a hydrogen atom initially and products would derive from there. (Scheme 2). We had recently reported the chemistry of series of dicarbomethoxy carbene precursors clearly demonstrated that manipulation of the thiophene portion of a series of sulfonium ylides could be used to change the initial spin state distribution of carbene generated on photolysis of the ylide from over 90% singlet to almost entirely triplet.²²⁻²³ The potential for analogous differentiation seemed plausible in this case.



Scheme 3. Potential primary reactivities for singlet and triplet alkyl oxenium ions

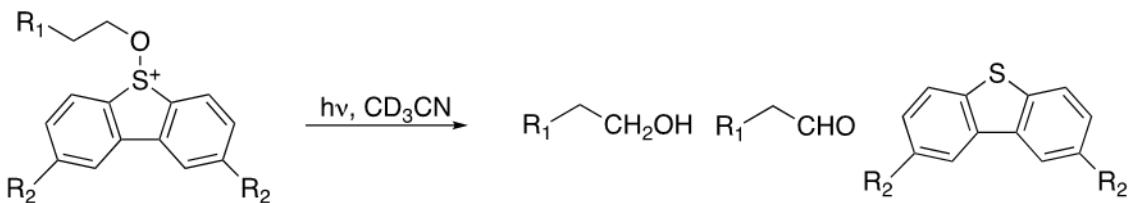
In contrast, photochemical homolysis of **1** or **2** would produce an alkoxy radical and DBT^{•+}. In-cage reaction of a singlet radical pair would also produce photoacid and aldehyde, presumably through transient formation of a protonated DBT. A triplet radical pair is subject to diffusive escape and it is presumed that the alkoxy radical would largely abstract hydrogen from the solvent, forming the observable alcohol. Depending on conditions, disproportionation might also lead to some aldehyde formation. Thus, it was clear that multiple experiments would be required to distinguish among the variables of spin multiplicity and heterolytic vs homolytic cleavages.

As an example of a known and analogous homolytic photolysis, the brief study of the alkoxy pyridines described herein was completed. Katritzky and Lunt reported the synthesis of *t*-butoxy pyridinium perchlorate, and their method was used to prepare the pyridinium perchlorates of primary, secondary, and tertiary derivatives.³⁹

3.3.2 Results of photolysis product study

Direct photolysis of *S*-ethoxy dibenzothiophenium salt **1a** at 350 nm in deuterated acetonitrile generates a 2:1 mixture of ethanol and acetaldehyde, as shown in Table 1. The overall yield of these two compounds, as determined by careful NMR integration relative to an internal standard, was 33% (relative to disappearance of **1a**) and was accompanied by a corresponding amount of **DBT**. In addition to ethanol and acetaldehyde, a third product was identified by a sharp NMR singlet at 5.45 ppm. This was confirmed to be ethylene with an authentic sample. Based on the integration, a yield of ethylene was approximately 15% was observed; we recognize that this does not include any ethylene that evolved into the gas phase. Numerous small peaks in the aromatic region indicated that several aromatic compounds were also observed, but these could not be identified. (No sulfoxide was observed in this or any case reported in Table 1. Additionally, the yields of **DBT** or its brominated derivative corresponded well to the observed quantity of alcohol and aldehyde.) Control experiments showed that the yield curves were relatively linear with conversion and that acetaldehyde would not be converted photochemically to ethanol under these conditions. A quantum yield for the formation of both alcohol and aldehyde of 0.12 was determined, which could be converted to 0.36 for the photochemical loss of the starting material **1a**.

The formation of an alkene product was not observed in any other photolysis and the pathway that leads to it remains unclear. It is tempting to suggest that a homolytic photochemical C-O cleavage occurs, but we have no evidence for this; no build-up of the corresponding sulfoxide was observed. Moreover, that would not explain why it is not observed on the photolysis of **2a** (see below).

Table 1. Photolysis of S-alkoxy dibenzothiophenium derivatives

Compound	R ₁	R ₂	λ, nm	Sens ^a	Total yield ^b	R ₁ OH: RCHO	Φ ^c
1a	H	H	350		33% ^d	67:33	0.12 ± 0.03
1a	H	H	285	DBT	75%	82:19	
1b	H	Br	254		64%	83:17	0.34 ± 0.06
1b	H	Br	350		36%	29:71	
2a	PhCH ₂	H	300		67%	88:12	
2a	PhCH ₂	H	264	PMA	86%	89:11	
2b	PhCH ₂	Br	254		66%	78:22	

^a PMA = *p*-methoxyacetophenone; DBT = dibenzothiophene. ^b Yield based on the sum of ROH and RCHO. The yield of **DBT** was always consistent with these values. ^c Quantum yield of the appearance of [ROH + RCHO]. Quantum yield of the disappearance of starting material is thus 0.36 and 0.53, respectively. ^d Additionally, ethylene was observed. See the main text.

We recently reported the photochemistry of series of dicarbomethoxy carbene precursors clearly demonstrating that manipulation of the thiophene portion of a series of sulfonium ylides could be used to change the initial spin state distribution of the carbene population generated on photolysis of the ylide from over 90% singlet to almost entirely triplet.²³ However, we later determined that DBT, which accumulates under photolysis conditions, can act as a triplet sensitizer.²² Thus photolysis of **1a** was carried out with **DBT** intentionally added to the solution and the excitation adjusted such that at least 90% of the light was absorbed by the sensitizer. Two significant changes were noted that indicate that the same phenomenon is observed here.

First, the total yield of the alcohol and aldehyde rose significantly to 75%, and no ethylene formation was observed. Second, there was a modest increase in the ratio of alcohol to aldehyde from approximately 2:1 to 4:1. The most straightforward interpretation here is that the formation of the ethylene (by whatever mechanism) does not pass through the lowest reactive triplet of **1a** and that indeed the formation of ethanol is indicative of triplet cleavage.

In part to look for a more easily observed and quantified alkene (i.e., allylbenzene), photolysis of a phenylpropyl derivative **2a** was carried out. No allylbenzene (or ethylene) was observed and an increase in the overall yield of alcohol and aldehyde was noted. A slight increase in the alcohol: aldehyde ratio, relative to direct photolysis of **1a**, was observed. Sensitization with *p*-methoxyacetophenone rather than DBT was chosen for practical reasons, but the effect was not dramatic as for **1a**, as reported in Table 1.

The sensitized photolysis results supported the hypothesis that the alcohol product derives from a triplet reactive intermediate, whether alkoxyl radical or oxenium ion. Introducing bromine to the arene of photochemical precursor has been observed in others of our works to induce triplet processes to varying degrees.^{20, 23, 40-41} Thus compounds **1b** and **2b** were also prepared and photolyzed. The observed yield of alcohol and aldehyde was low for 350 nm photolysis of **1b** (again, without observation of ethylene).

In the photolysis of dibenzothiophene sulfoxide, a distinct wavelength dependence is known.⁴² Thus, for this compound whose 350 nm photolysis did not fit the previous pattern, the 254 nm photolysis was also examined. A similar observation was made here, where the short wavelength irradiation produced both a higher overall yield and a higher relative percentage of alcohol. The quantum yield for product formation and loss of starting material are 0.34 and 0.56, respectively. Results for **2b** photolyzed at 254 nm were essentially identical to those for **1b**.

The data in Table 1 are consistent with a modest heavy atom effect. These results are reasonably consistent with the simplest possible hypothesis that any singlet cleavage gives rise to the aldehyde and triplet cleavage gives rise to the alcohol. However, a better fit may come from the additional allowance that alkoxy radicals may disproportionate under these conditions, which produces a baseline amount of the aldehyde (probably 15-20%, relative to the alcohol), present regardless of whether any singlet cleavage is taking place.

Photolysis of **1a** in CD₃CD₂OD supports this hypothesis. In this case, only ethanol was observed by NMR. No acetaldehyde nor its diethyl acetal was detected. It stands to reason that, as ethanol is a better hydrogen atom donating solvent than acetonitrile, the nascent ethoxy radicals are resolved into ethanol before disproportionating with one another. (The deuterated nature of the solvent ethanol naturally means we are blind to the resulting radical products of the deuterated radicals.)

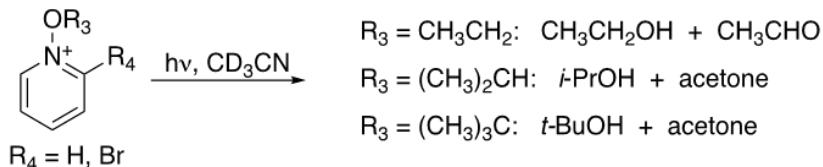
In order to explore this further, we wished to explore photolysis sulfonium ylides based on secondary or tertiary alcohols. However, as noted previously, we found that such S-alkoxy dibenzothiophenium salts could not be isolated and those efforts were frustrated.³⁷⁻³⁸

As a backup position, the photolysis of a few *N*-alkoxy pyridinium perchlorates (**3a**, **3b**, **4**, **5**) was explored. These compounds are widely viewed as producing alkoxy radicals and pyridinium radical cations on direct photolysis.^{28-30, 32-33, 39} Experiments analogous to those described above were carried out with these compounds and are reported in Table 2. Since acid is generated, the resulting insoluble pyridinium salts were not quantified.

In this instance, inserting a Br into compound **3a** to give **3b** resulted in the only instance we report here in which aldehyde was not observed. (Other than that photolysis of **3a** did not

result in the formation of ethylene), the observed ~4:1 ratio of alcohol to aldehyde and middling yields were in qualitative agreement with those of the sulfur compounds. Switching the alkyl group to isopropyl gave our second instance of more ketone (acetone) than alcohol (isopropyl

Table 2. Photolysis of N-alkoxy pyridinium perchlorates



Compound	R3	R4	λ, nm	Total yield ^a	R ₁ OH: C=O	Φ ^c
3a	CH ₃ CH ₂	H	254	35%	78:22	0.15 ± 0.03
3b	CH ₃ CH ₂	Br	254	56%	100:0	0.18 ± 0.04
4	(CH ₃) ₂ CH	H	254	35%	25:75	0.16 ± 0.16
5	(CH ₃) ₃ C	H	254	70%	24:76	0.090 ± 0.007

^a Yield based on the sum of ROH and RCHO. ^b Note that the carbonyl compound is acetaldehyde for **3**, and acetone for **4** and **5**. ^c Quantum yield of the appearance of [ROH + C=O]. Quantum yield of the disappearance of starting material is thus 0.43, 0.32, 0.46, and 0.13, respectively.

alcohol), without otherwise dramatically changing the observed parameters. With the alkyl group set as *t*-butyl, acetone is also observed.³¹ However, this is almost certainly due to secondary fragmentation of a *t*-BuO• radical (and clearly not disproportionation). While not dispository, the similar results between these compounds and the sulfur analogs certainly are suggestive that a similar mechanism is in play, i.e., S-O and N-O homolysis.

3.3.3 Additional results supporting homolytic cleavage.

In a recent publication, Winter and coworkers reported the direct observation of a triplet aryloxenium ion by epr at near liquid-He temperatures.³ (The use of literally the same

instrumentation that had previously successfully detected a triplet oxenium was a fortuitous control for sensitivity.) Photolysis of **1a** in a variety of solvents did not result in the observation of any high spin compounds at 10 K. However, large spin-1/2 signals were observed. While this is the lack of evidence for the oxenium, rather than specific evidence against the oxenium, it is consistent with the homolytic pathway for **1a**.

Finally, the photolysis of **1a** and **2a** was also carried out in O₂-saturated acetonitrile. Numerous analogous control photolysis with **DBT** (or its sulfoxide, sulfilimines, and sulfonium ylides upon which we have previously reported) show no oxidation of the DBT nucleus when oxygen is present. That is, in all these cases, **DBT** is the end point of the sulfur bearing component, regardless of the presence or absence of molecular oxygen. However, Che and coworkers have previously shown that DBT is oxidized by O₂ when its radical cation is formed (in their case by photoinduced electron transfer to N-methyl quinolinium).⁴³ In O₂-saturated acetonitrile, photolysis of **1a** and **2a** resulted in sulfide:sulfoxide:sulfone ratios of 59:31:10 and 43:46:11, respectively. We do not ascribe any significance to the relatively minor difference in observed ratios here, but rather interpret this to mean that **DBT**⁺ is clearly present in the reaction pathway.

3.4 Conclusion

This report represents the first instance we have reported in which S-functionalized derivatives of dibenzothiophene undergo photo-homolysis rather than photo-heterolysis. In this fashion, S-alkoxy dibenzothiophenium salts behave more like traditional sulfonium salts than they do like the sulfoxides and sulfilimines. Evidence is strongly in favor of radical-and-DBT⁺ formation, though some fraction of oxenium-and-DBT cannot be ruled out. Similarly, the simplest hypothesis to account for the formation of aldehydes in these reactions is that there are two sources: (a) geminate reaction of an alkoxy radical and DBT⁺ presumably of singlet

multiplicity; and (b) disproportionation of freely diffusing alkoxy radicals which are presumably largely from triplet homolysis.

3.5 Experimental section

Compounds.

All new compounds were characterized by ^1H and ^{13}C NMR and by HRMS (ESI).

Spectra are given in supporting material.

General method of synthesis of S-Alkoxy dibenzothiophenium tetrafluoroborates (1a, 2a).

To a solution of dibenzothiophene-S-oxide (2.0 mmol) in about 20 mL of dichloromethane in a 100 mL round bottomed flask, the corresponding alkyl iodide or alkyl bromide (1.1 equiv) and AgBF_4 (1.1 equiv) were added and the mixture was stirred overnight. The next day, the precipitate of silver halide was filtered off, and diethyl ether was added to the remaining solution to precipitate the product. The precipitated product was collected by filtration and rinsing. No further purification was needed. Yields were in the range of 40–60%.³⁶

S-Ethoxy dibenzothiophenium tetrafluoroborate (1a). Yield: 60%. ^1H NMR (400 MHz, CD_3CN): δ 8.30 (d, $J = 7.9$ Hz, 2H), 8.17 (d, $J = 7.7$ Hz, 2H), 7.99 (t, $J = 8.2$ Hz, 1H), 7.78 (t, $J = 8.3$ Hz, 1H), 3.84 (q, $J = 7.0$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (400 MHz, CD_3CN): δ 140.64, 137.61, 131.88, 130.59, 129.16, 124.33, 70.40, 14.29. HR-MS (ESI): Calculated mass: 229.0682, Found: 229.0682.

S-(3-Phenylpropyl) dibenzothiophenium tetrafluoroborate (2a), Yield: 64%. ^1H NMR (400 MHz, CD_3CN): δ 8.30 (d, $J = 0.6$ Hz, 2H), 8.14 (d, $J = 0.6$ Hz, 2H), 7.98 (td, $J = 7.7, 1.1$ Hz, 2H), 7.77 (td, $J = 7.7, 1.1$ Hz, 2H), 7.25 (t, $J = 7.8$ Hz, 2H), 7.18 (t, $J = 6.7$ Hz, 1H), 7.08 (d, $J = 7.2$ Hz, 2H), 3.66 (t, $J = 6.1$ Hz, 2H), 2.58 (t, $J = 7.5$ Hz, 2H), 1.94 – 1.83 (m, 2H). ^{13}C NMR

(400 MHz, CD₃CN): δ 140.72, 140.23, 137.64, 131.88, 130.67, 128.80, 128.49, 128.32, 126.21, 124.31, 72.10, 30.56, 30.10. HR-MS (ESI): Calculated mass: 319.1151, Found: 319.1158.

General method of synthesis of S-Alkoxy 2,8-dibromodibenzothiophenium tetrafluoroborate (1b, 2b).

To a solution of 3,7-dibromodibenzothiophene-S-oxide (2 mmol) in about 20 mL of 1,2-dichloroethane in a 100 mL round bottomed flask, 1-bromo-3-phenylpropane (2.5 equiv) and AgBF₄ (2.5 equiv) were added and the mixture was stirred overnight. The next day, the precipitated silver halide was filtered off, and diethyl ether was added to the remaining solution to precipitate the product. The precipitated product was collected by filtration and rinsing. This compound contained a small percentage ≤ 4% of the corresponding sulfoxide.

S-Ethoxy 2,8-dibromodibenzothiophenium tetrafluoroborate (1b). Yield: 38%. ¹H NMR (400 MHz, CD₃CN): δ 8.40 (d, *J* = 1.5 Hz, 2H), 8.20 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 1H), 3.84 (q, *J* = 7.0 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (400 MHz, CD₃CN): δ 141.22, 135.32, 132.58, 131.81, 128.64, 128.21, 71.21, 14.28. HR-MS (ESI): Calculated mass: 384.8892, Found: 386.8879 (Mass of the middle peak of the dibromo triplet)

S-(3-Phenylpropyl) 2,8-dibromodibenzothiophenium tetrafluoroborate (2b). Yield: 35%. ¹H NMR (400 MHz, CD₃CN): δ 8.35 (d, *J* = 1.8 Hz, 2H), 8.17 (d, *J* = 8.5 Hz, 2H), 7.95 (dd, *J* = 8.4, 1.9 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 6.7 Hz, 2H), 3.68 (t, *J* = 6.2 Hz, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.94 – 1.85 (m, 2H). ¹³C NMR (400 MHz, CD₃CN): δ 141.27, 140.10, 135.32, 132.61, 131.83, 128.50, 128.39, 128.28, 128.17, 126.23, 72.83, 30.42, 30.01. HR-MS (ESI): Calculated mass: 474.9374, Found: 476.9356 (Mass of the middle peak of the dibromo triplet)

General method for *N*-alkoxy pyridinium perchlorate derivatives.

The method of Katritzky and Lunt was used to prepare these compounds.³⁹ The *N*-t-butoxy pyridinium perchlorate was a known compound whose spectra were confirmed. The others were characterized by NMR and HRMS (ESI)

N-Ethoxy pyridinium perchlorate (3a). Yield: 10%. ¹H NMR (400 MHz, CD₃CN): δ 8.96 (d, *J* = 5.9 Hz, 2H), 8.60 – 8.52 (m, 1H), 8.18 – 8.11 (m, 2H), 4.68 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (400 MHz, CD₃CN): δ 145.44, 141.48, 129.66, 80.26, 12.40. HR-MS (ESI): Calculated mass: 124.0757, Found: 124.0753.

N-Ethoxy 2-bromopyridinium perchlorate (3b). Yield: 10%. ¹H NMR (400 MHz, CD₃CN): δ 9.09 (d, *J* = 6.6 Hz, 1H), 8.37 (d, *J* = 4.8 Hz, 2H), 8.13 – 8.05 (m, 1H), 4.67 (q, *J* = 7.0 Hz, 2H), 1.54 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (400 MHz, CD₃CN): δ 145.79, 144.23, 136.26, 134.96, 128.51, 80.24, 12.34. HR-MS (ESI): Calculated mass: 201.9862, Found: 201.9862.

N-isopropoxy pyridinium perchlorate (4). Yield: 20%. ¹H NMR (400 MHz, CD₃CN): δ 8.90 (d, *J* = 6.7 Hz, 2H), 8.61 – 8.54 (m, 1H), 8.14 (t, *J* = 7.2 Hz, 2H), 5.06 – 4.85 (m, 1H), 1.42 (d, *J* = 6.8 Hz, 4H). ¹³C NMR (400 MHz, CD₃CN): δ 145.51, 142.10, 129.60, 88.08, 19.34. HR-MS (ESI): Calculated mass: 138.0913, Found: 138.0912.

General method of photolysis

A known amount of S-alkoxy dibenzothiophenium tetrafluoroborate or N-alkoxy pyridinium perchlorate was dissolved in 1 mL of CD₃CN. Initial concentrations were typically 20–40 mM. The solution was transferred to an NMR tube and closed with a rubber septum. Then, the solution was gently sparged with Ar gas for about 20 minutes. The deoxygenated

solution was photolyzed using a Rayonet lamp (Southern New England Ultraviolet, RMR-600, modified with a fan at the bottom) fitted with the UV bulbs of the appropriate wavelength (254 nm or the broad sources centered at 300 or 360 nm). The reaction was photolyzed to 100% conversion and monitored with $^1\text{H-NMR}$ using a suitable internal solvent. Reported yields are from at least triplicate runs. When a sensitizer was used, dibenzothiophene (DBT) or *p*-methoxyacetophenone (PMA) was added to the solution, otherwise using the same protocol. The concentration of sensitizer was adjusted so that $\geq 90\%$ of the light was absorbed by the sensitizer at the wavelength of irradiation.

Quantum yield Measurements

Quantum yields were measured relative to the photolysis of azoxybenzene as a chemical actinometer.⁴⁴ Azoxybenzene was photolyzed in a solution of ethanol and potassium hydroxide monitoring the appearance of 2-hydroxyazobenzene at 458 nm. The quantum yields of the appearance of the products of the photolysis of *S*-alkoxy dibenzothiophenium tetrafluoroborate and *N*-alkoxy pyridinium perchlorate were measured by photolysis using a 75 W Xenon arc lamp with a monochromator set at 254 nm (*ca.* 20 nm bandpass) for all precursors except *S*-ethoxy dibenzothiophenium tetrafluoroborate, which was done at 350 nm. Reported errors are standard deviations from at least triplicate runs. The reaction progress was monitored by $^1\text{H-NMR}$.

EPR experiments

1-2 mM solution of *S*-alkoxy dibenzothiophenium tetrafluoroborate or *N*-alkoxy pyridinium perchlorates was made in 1 mL of the solvent (Ethanol, dichloromethane, 1,1,2,2-tetrachloroethane) and transferred to an EPR tube. The tube is then frozen in liquid N₂ to make a glass matrix. Then the tube is into the sample probe (cooled to 77 K or 10 K) of the Bruker Elexsys E580 X-band FT-EPR spectrometer equipped with a UV accessory (Hg vapor lamp) and

a light pipe through which the sample is irradiated. The sample is irradiated for about half an hour and the EPR spectrum is acquired.

3.6 Acknowledgments

The authors thank Iowa State University for support of this work.

Supplementary Data

NMR spectra of previously unreported compounds and quantitative UV Spectra are provided in the supplementary data.

Supplementary data

NMR spectra of the synthesized compounds

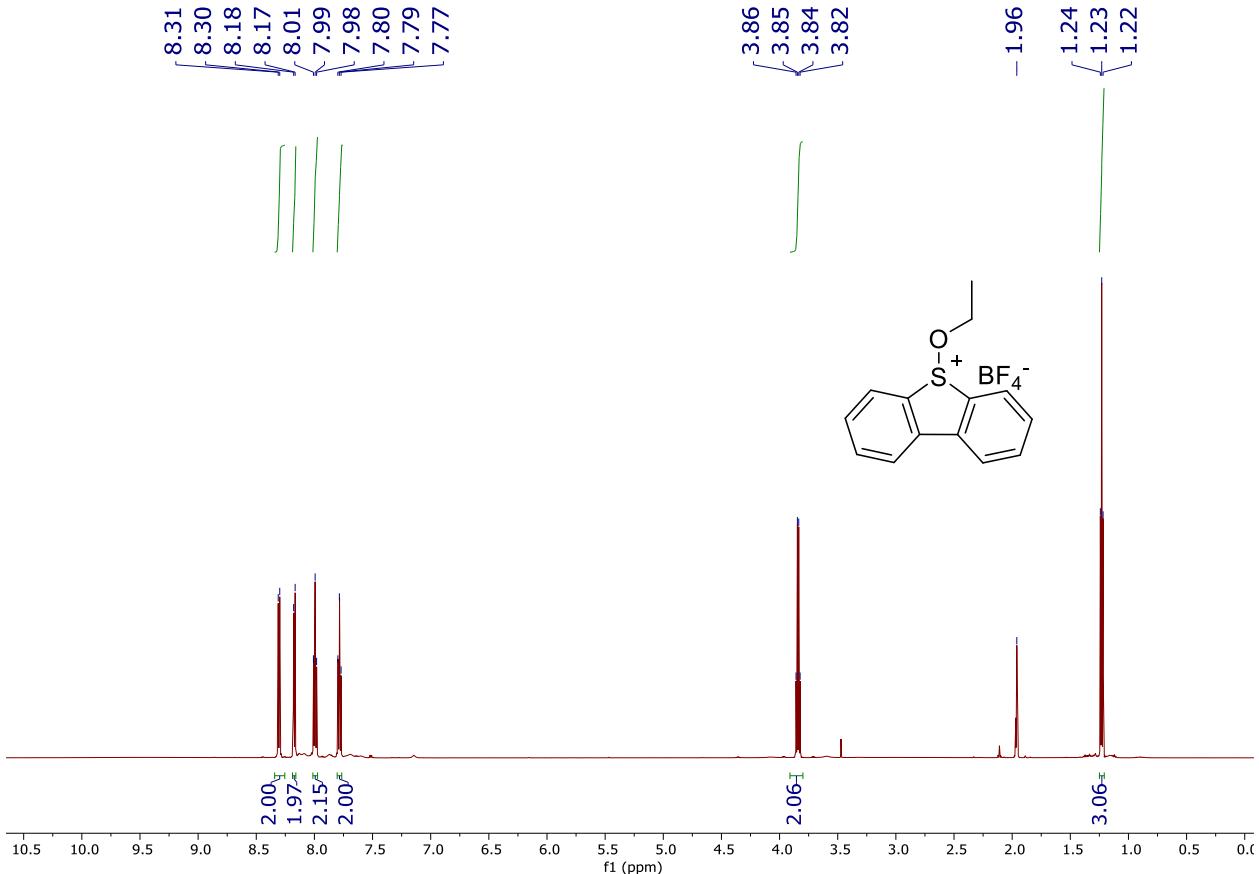


Figure S1. ¹H-NMR S-Ethoxy dibenzothiophenium tetrafluoroborate (1a).

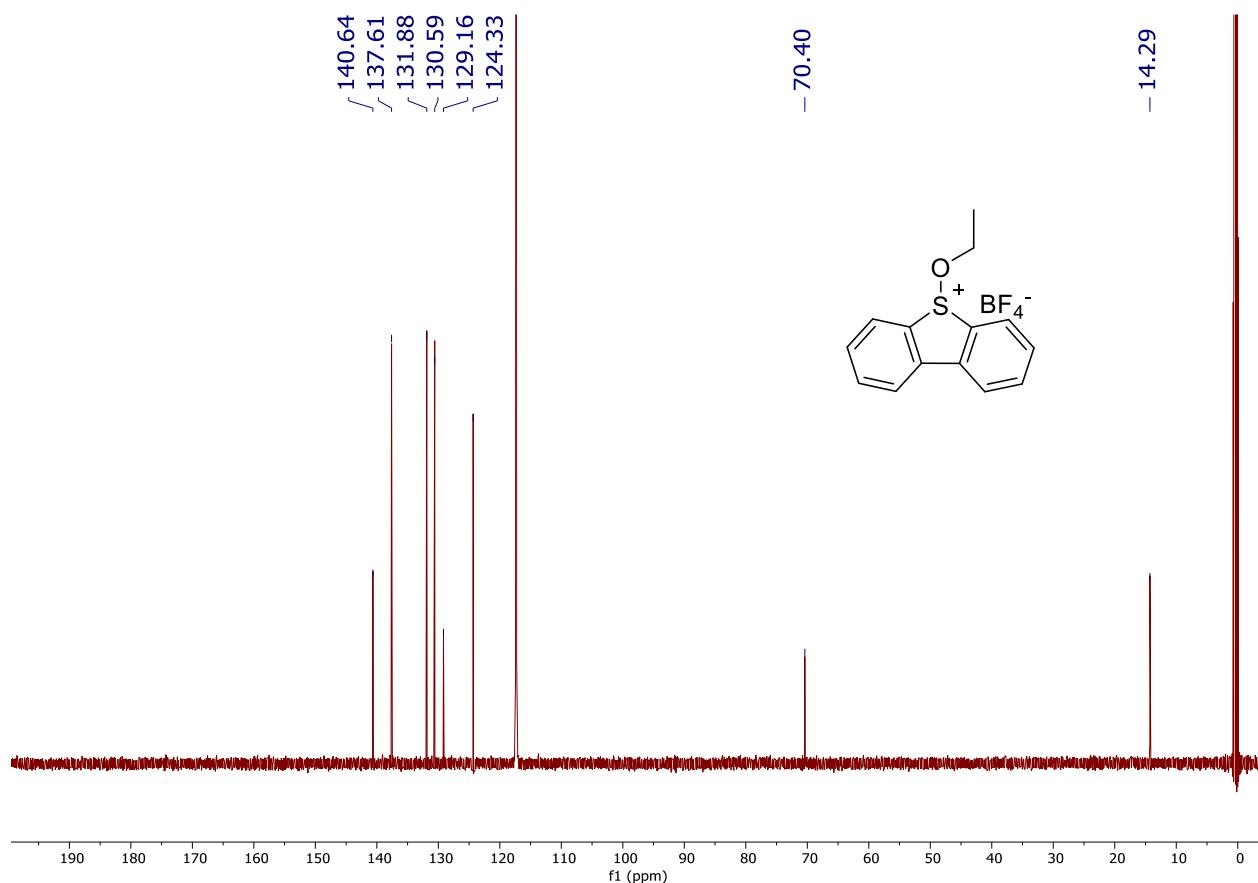


Figure S2. ^{13}C -NMR S-Ethoxy dibenzothiophenium tetrafluoroborate (1a).

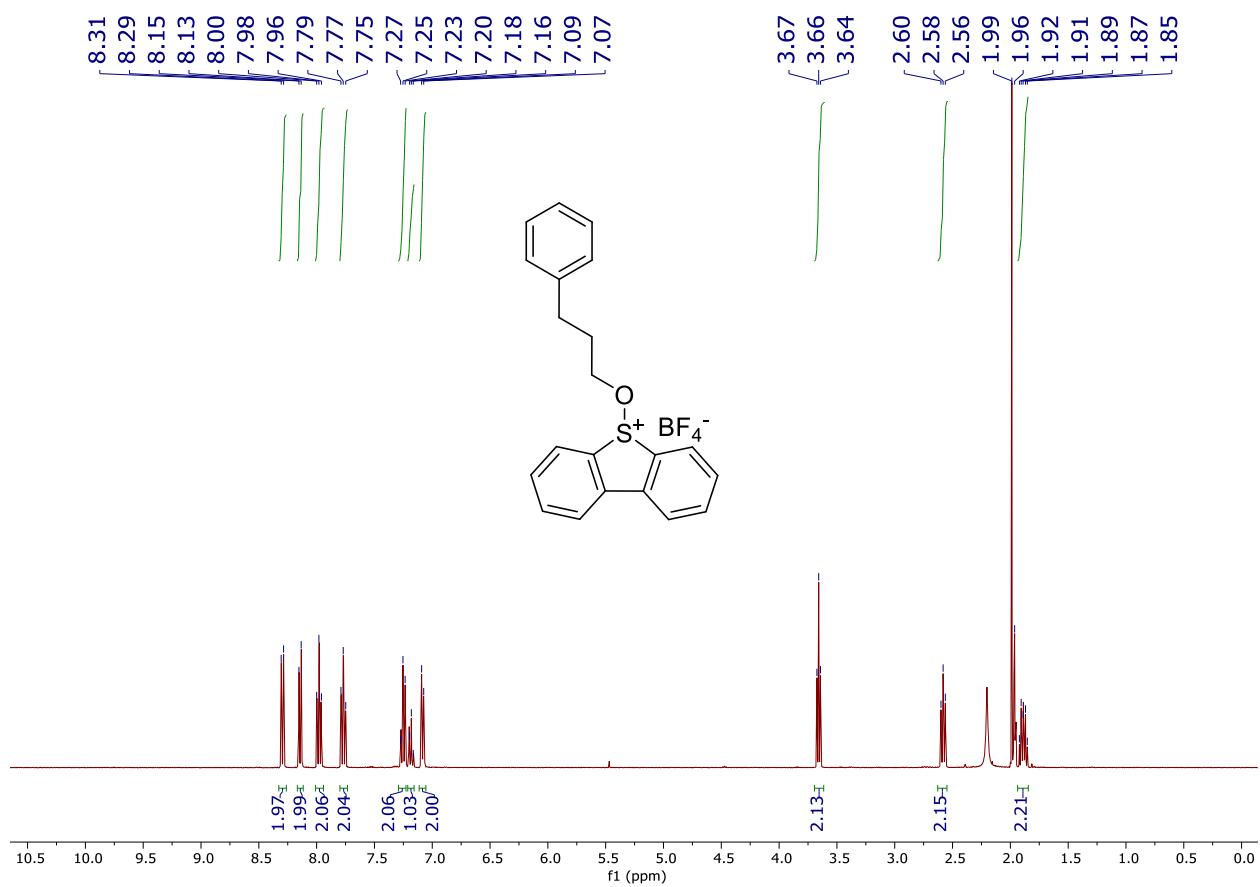


Figure S3. ¹H-NMR S-(3-Phenylpropyl) dibenzothiophenium tetrafluoroborate (2a).

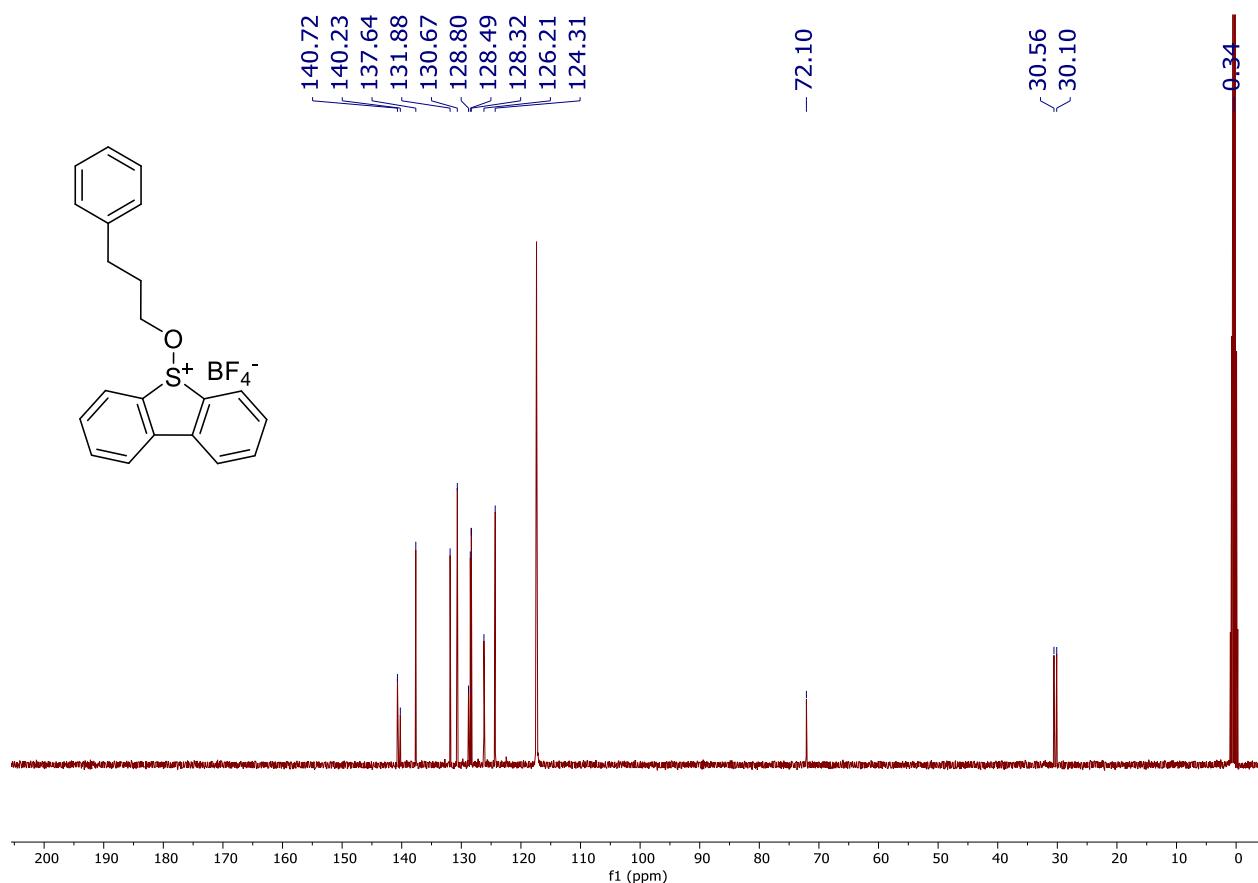


Figure S4. ^{13}C -NMR S-(3-Phenylpropyl) dibenzothiophenium tetrafluoroborate (2a).

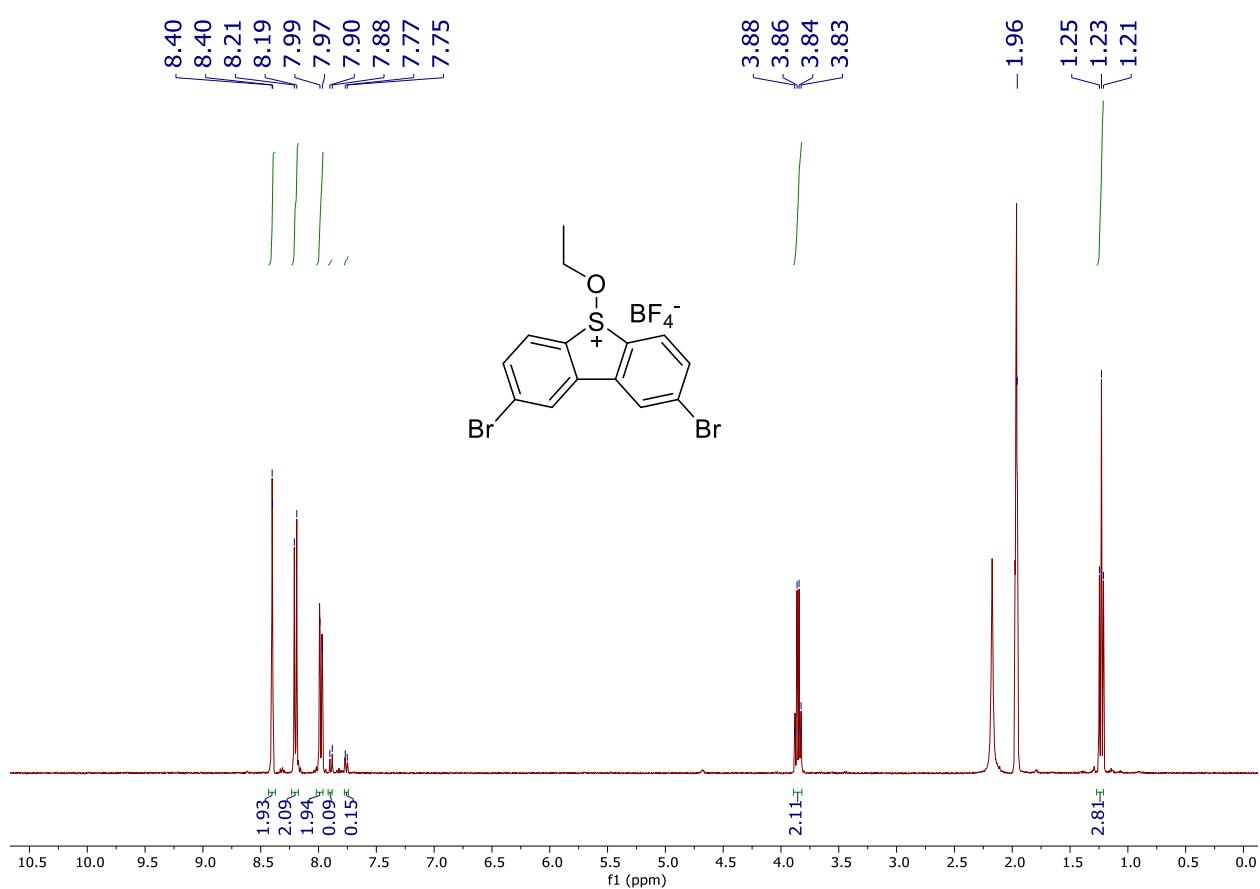


Figure S5. ¹H-NMR S-Ethoxy 2,8-dibromodibenzothiophenium tetrafluoroborate (1b).

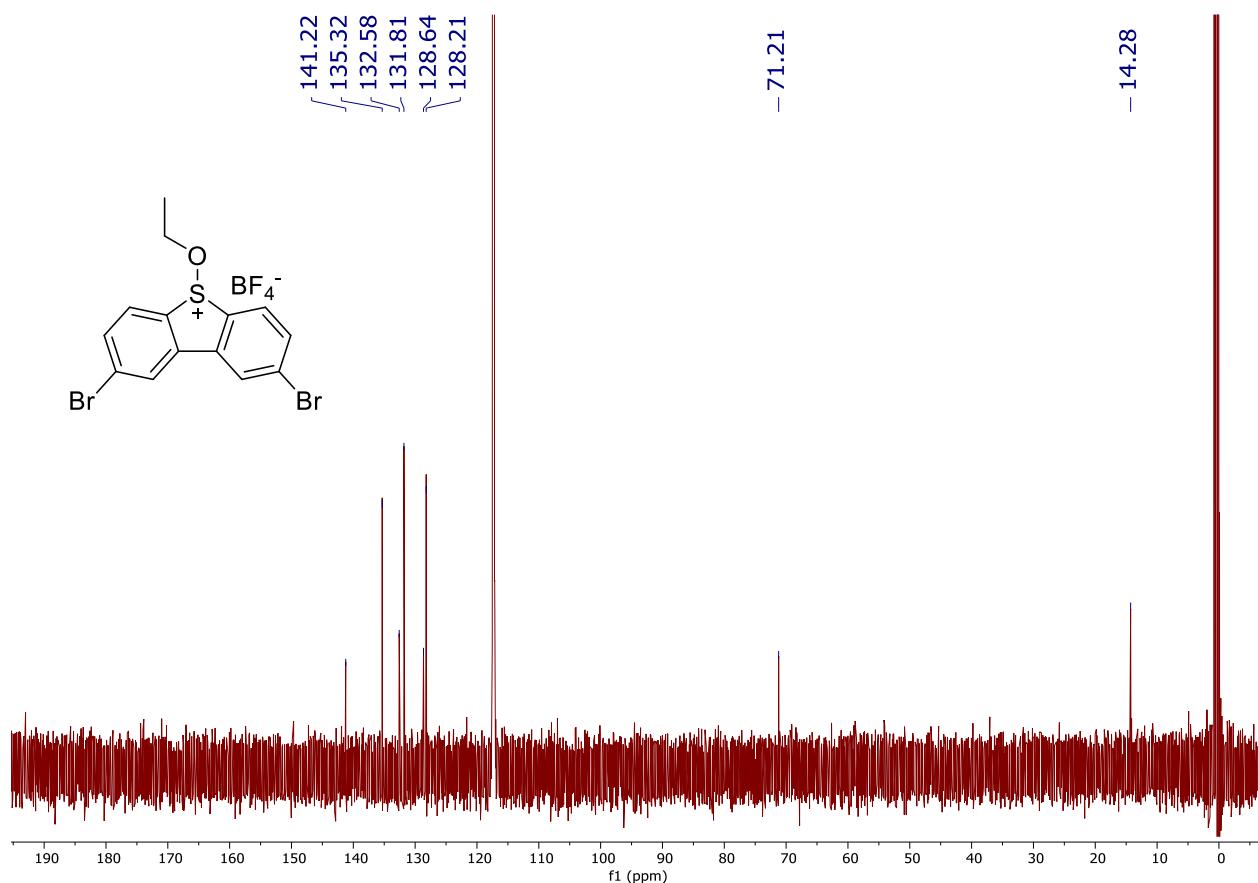


Figure S6. ^{13}C -NMR S-Ethoxy 2,8-dibromodibenzothiophenium tetrafluoroborate (1b).

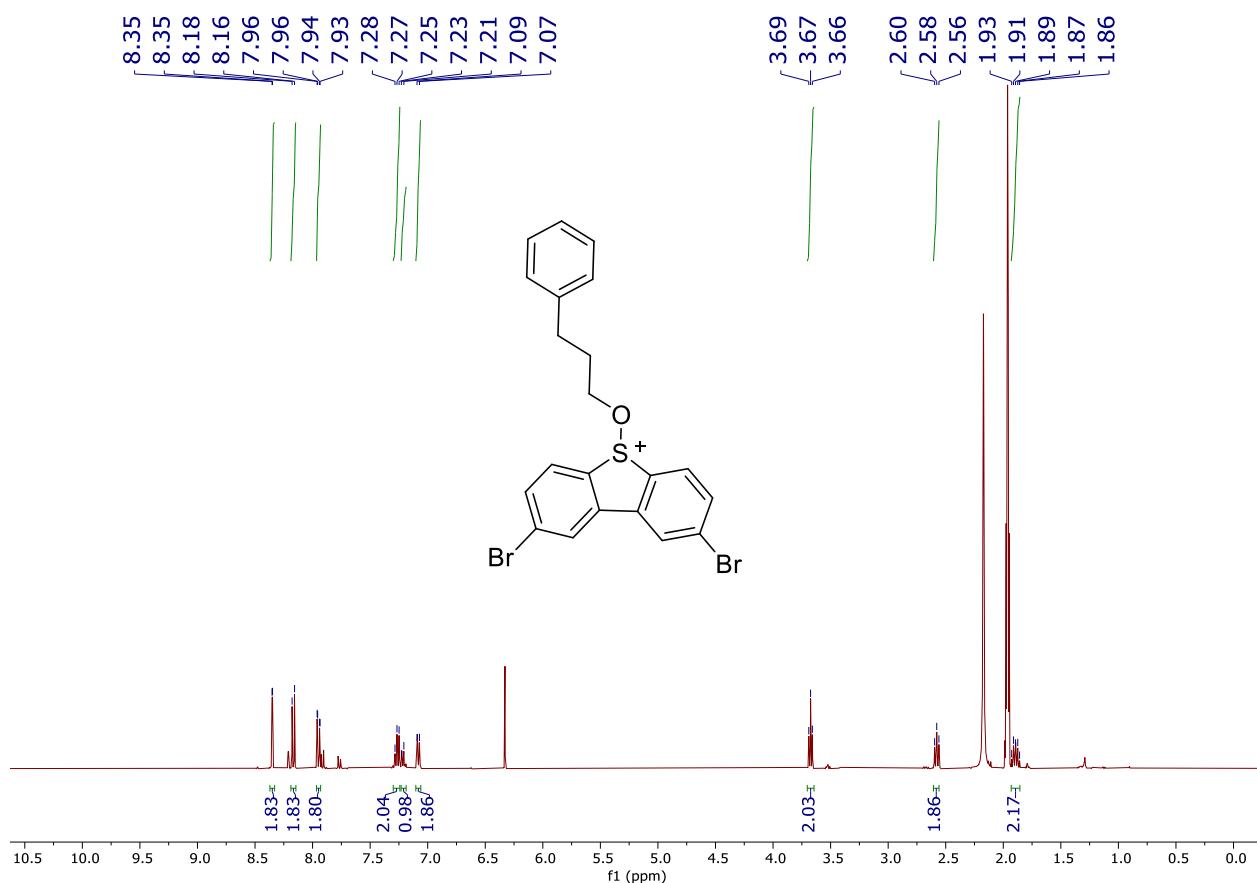


Figure S7. ¹H-NMR S-(3-Phenylpropyl) 2,8-dibromodibenzothiophenium tetrafluoroborate (2b).

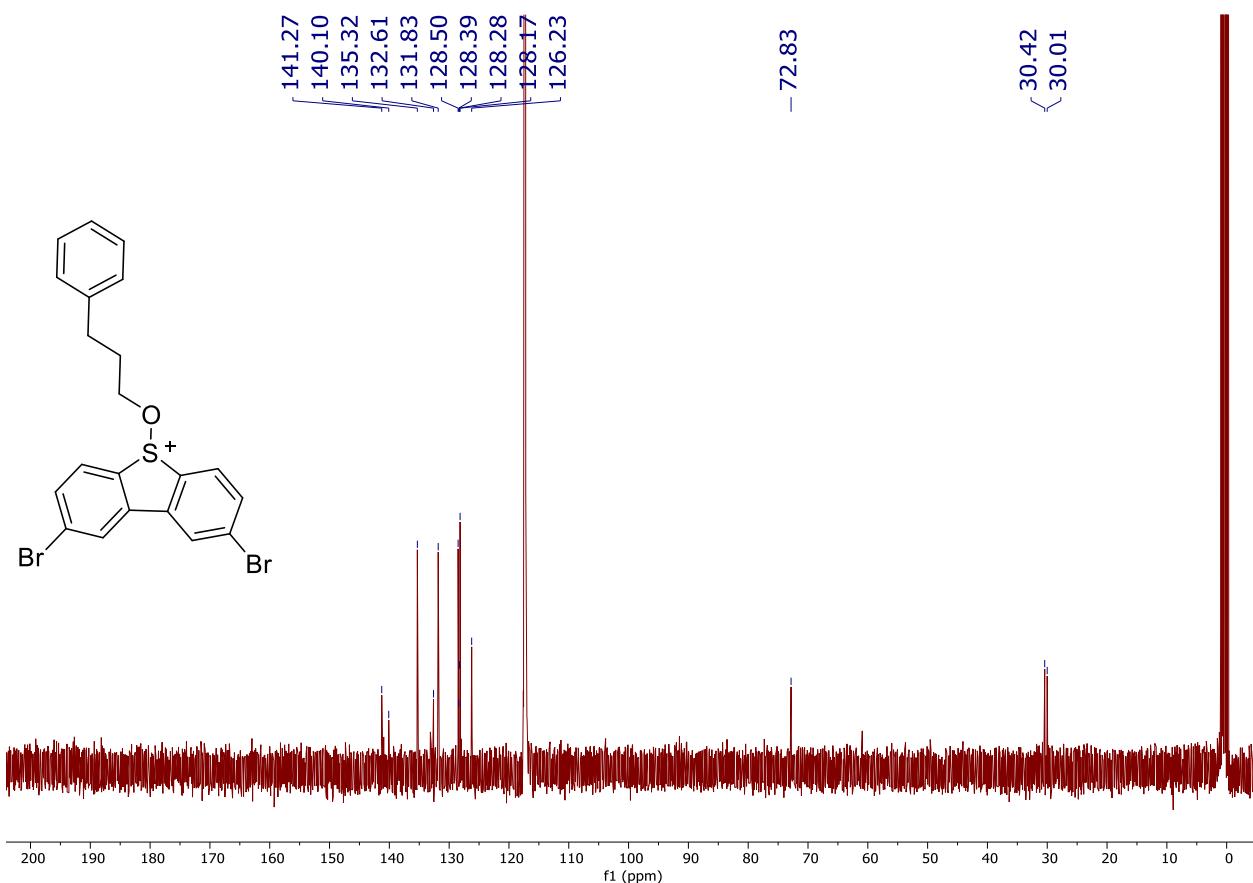


Figure S8. ^{13}C -NMR S-(3-Phenylpropyl) 2,8-dibromodibenzothiophenium tetrafluoroborate (2b).

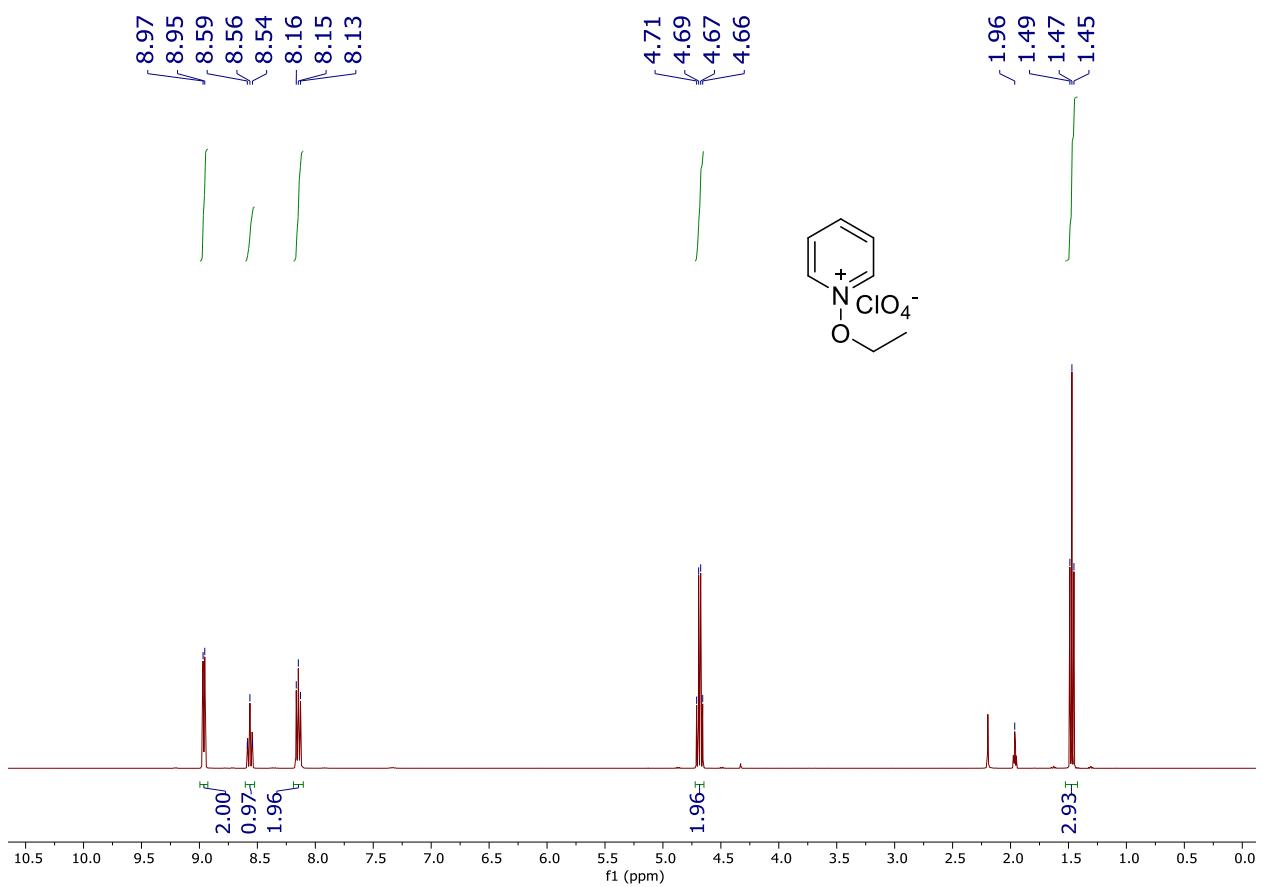


Figure S9. ^1H -NMR N-Ethoxy pyridinium perchlorate (3a).

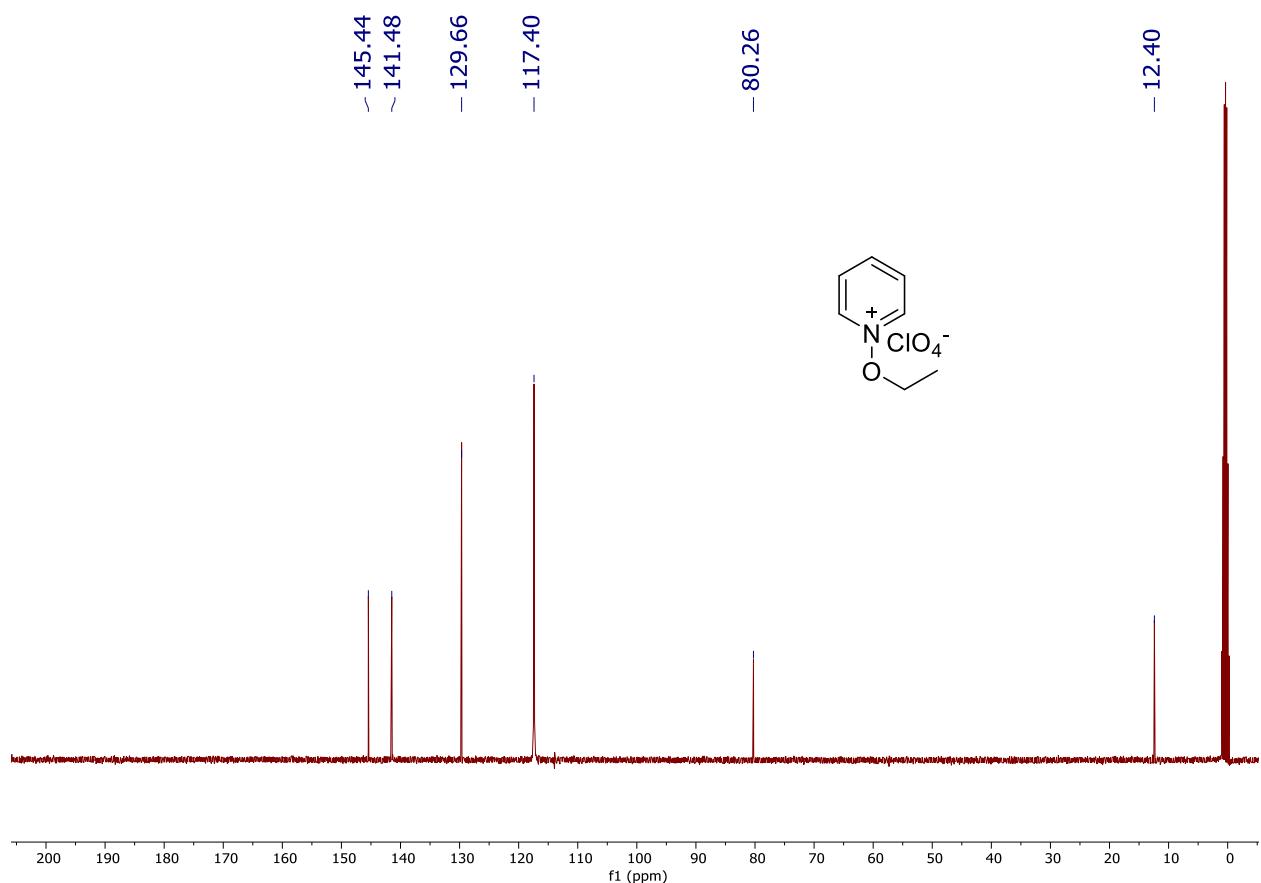


Figure S10. ^{13}C -NMR N-Ethoxy pyridinium perchlorate (3a).

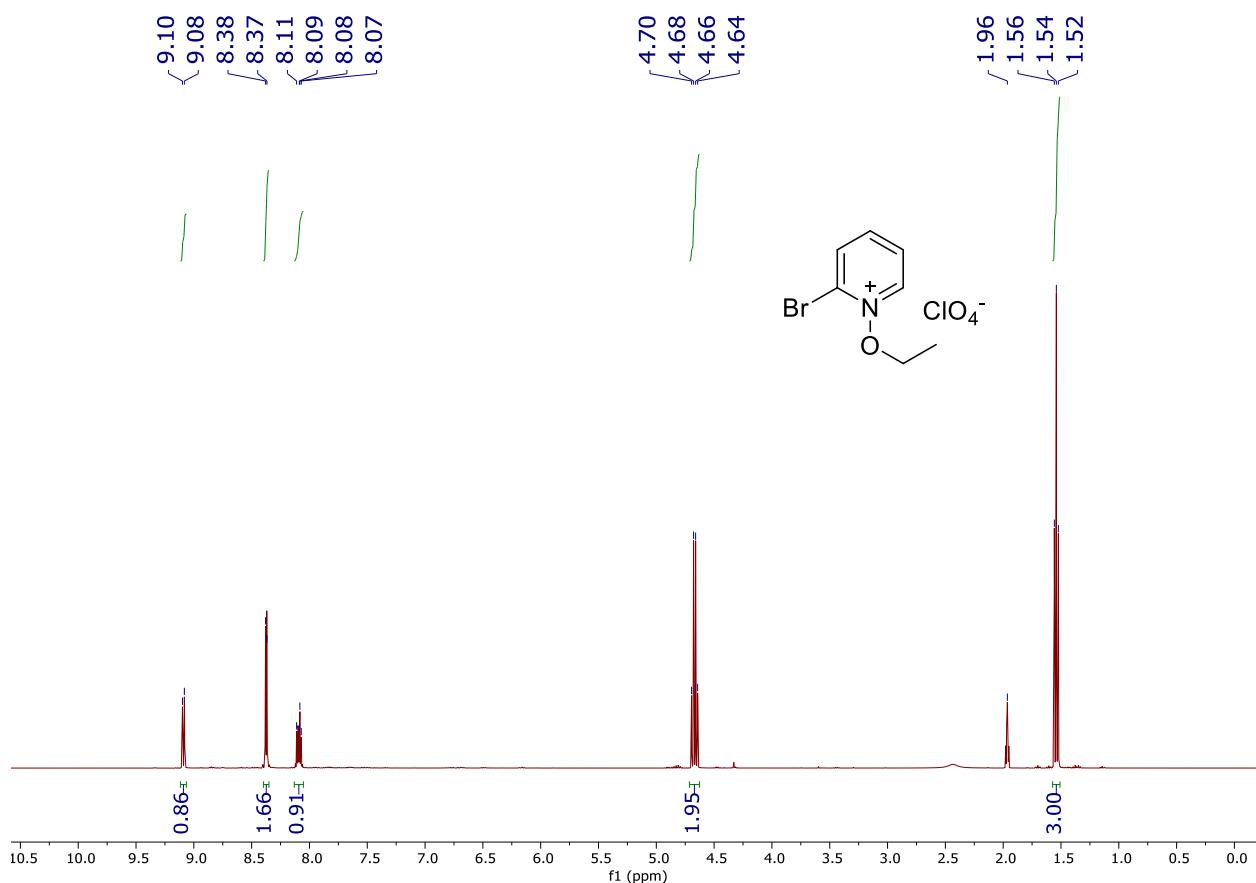


Figure S11. ^1H -NMR N-Ethoxy 2-bromopyridinium perchlorate (3b).

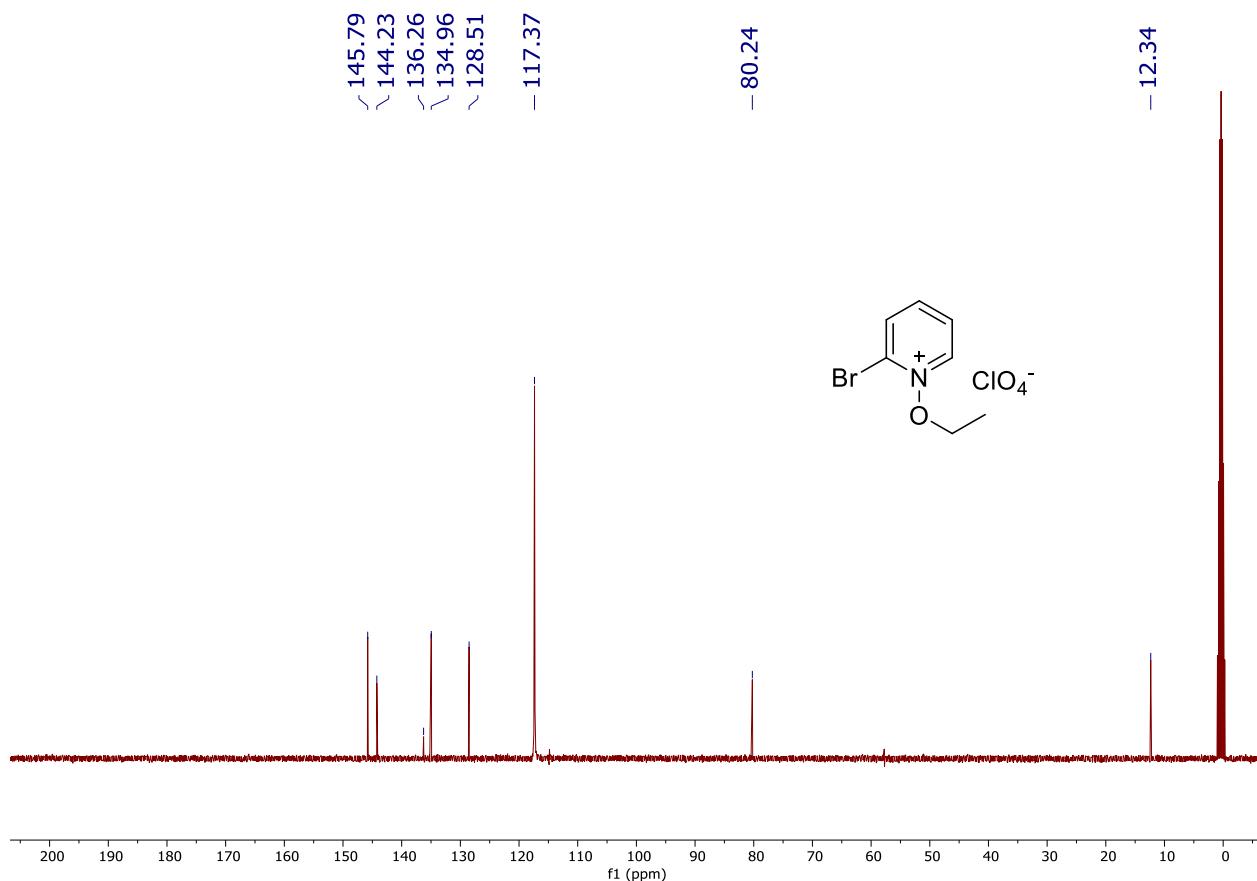


Figure S12. ^{13}C -NMR N-Ethoxy 2-bromopyridinium perchlorate (3b).

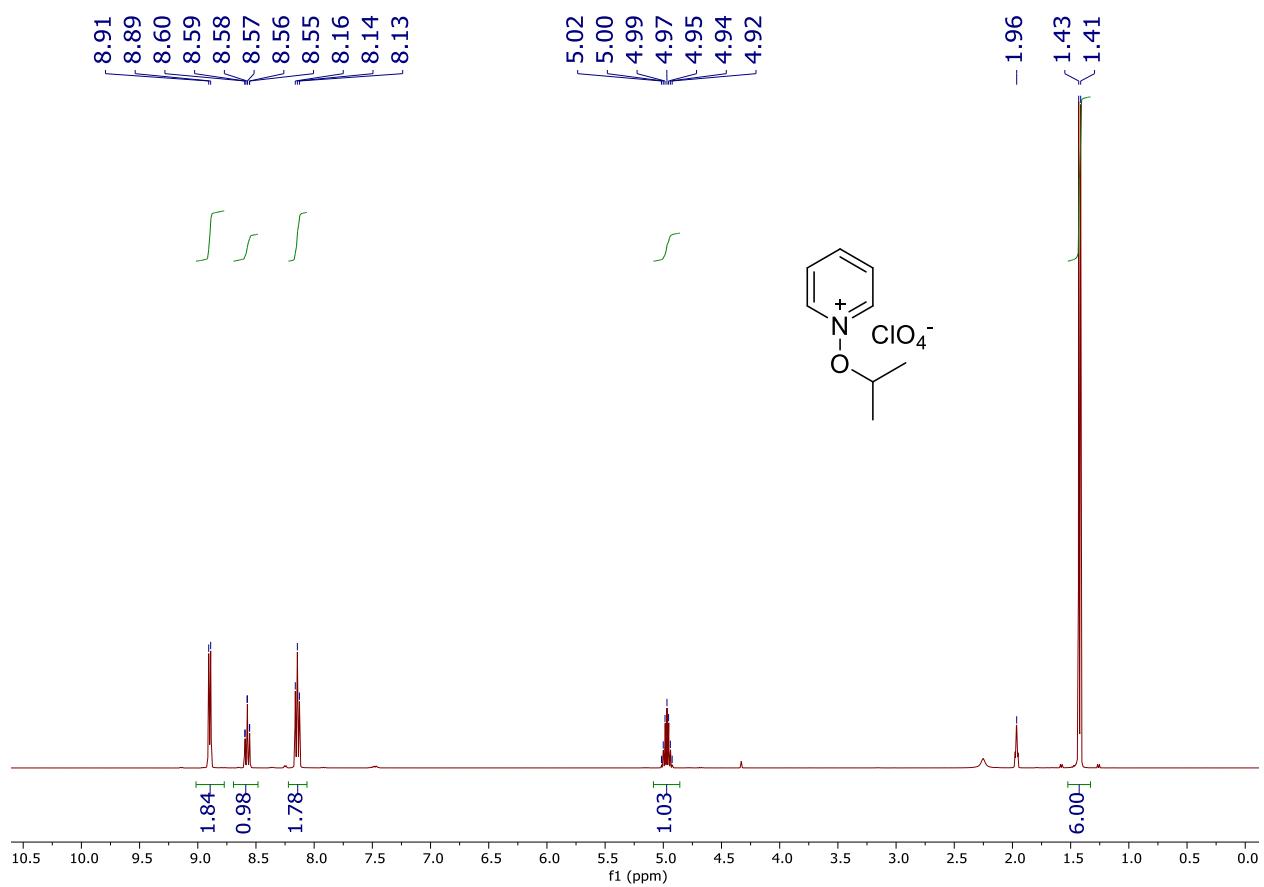


Figure S13. ^1H -NMR N-isopropoxy pyridinium tetrafluoroborate (4).

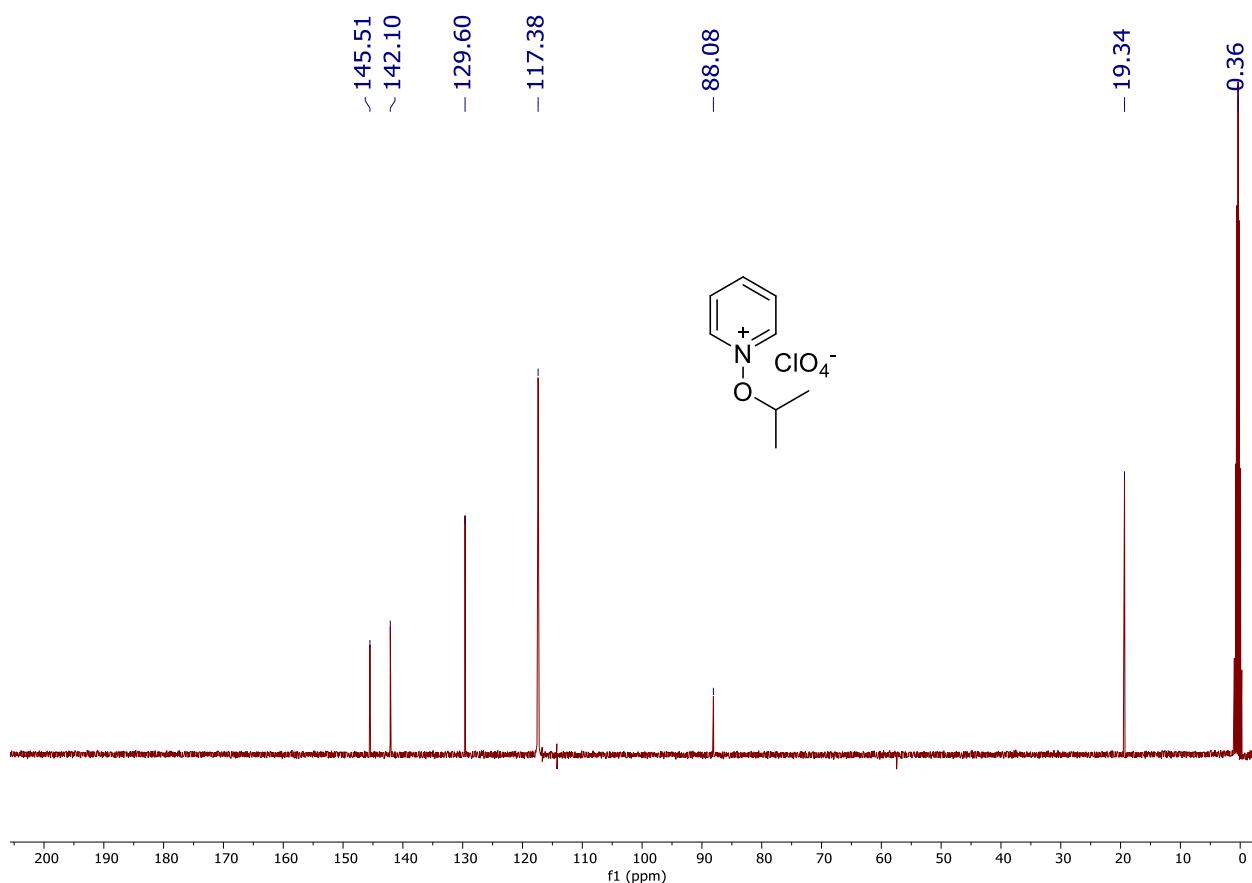


Figure S14. ^{13}C -NMR N-isopropoxy pyridinium tetrafluoroborate (4).

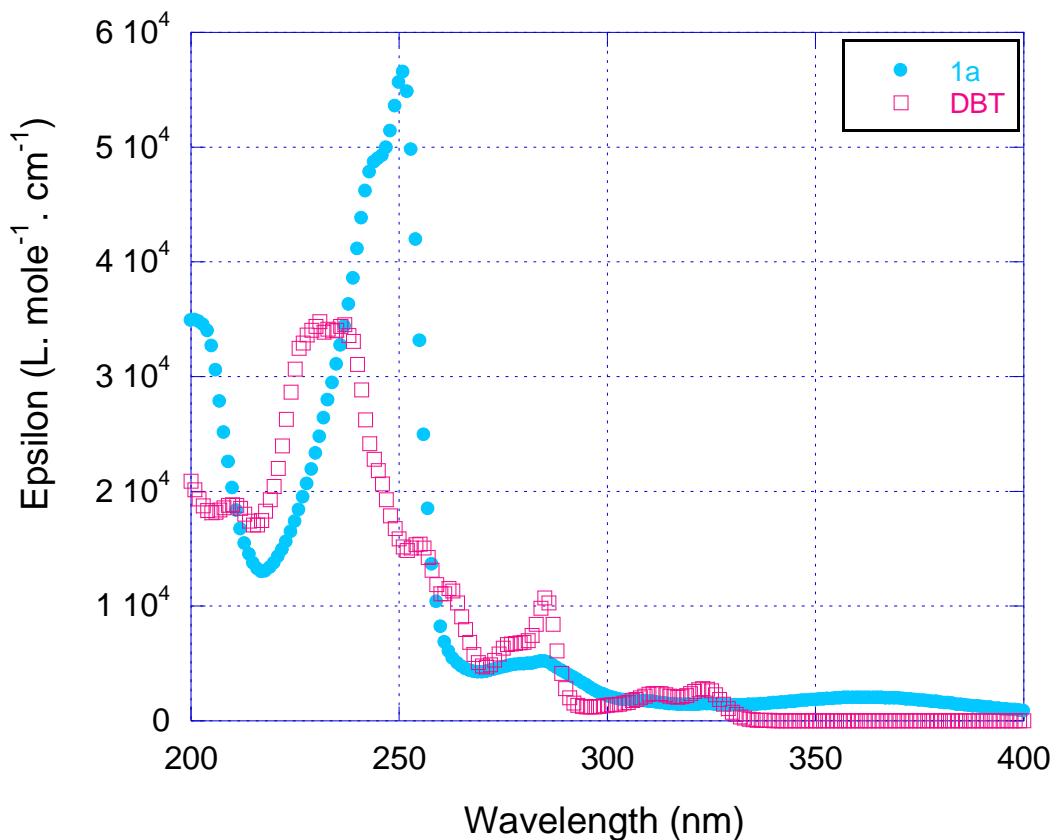
Quantitative UV-Vis Spectra

Figure S15. UV absorption spectra of S-Ethoxy dibenzothiophenium tetrafluoroborate (1a) and DBT.

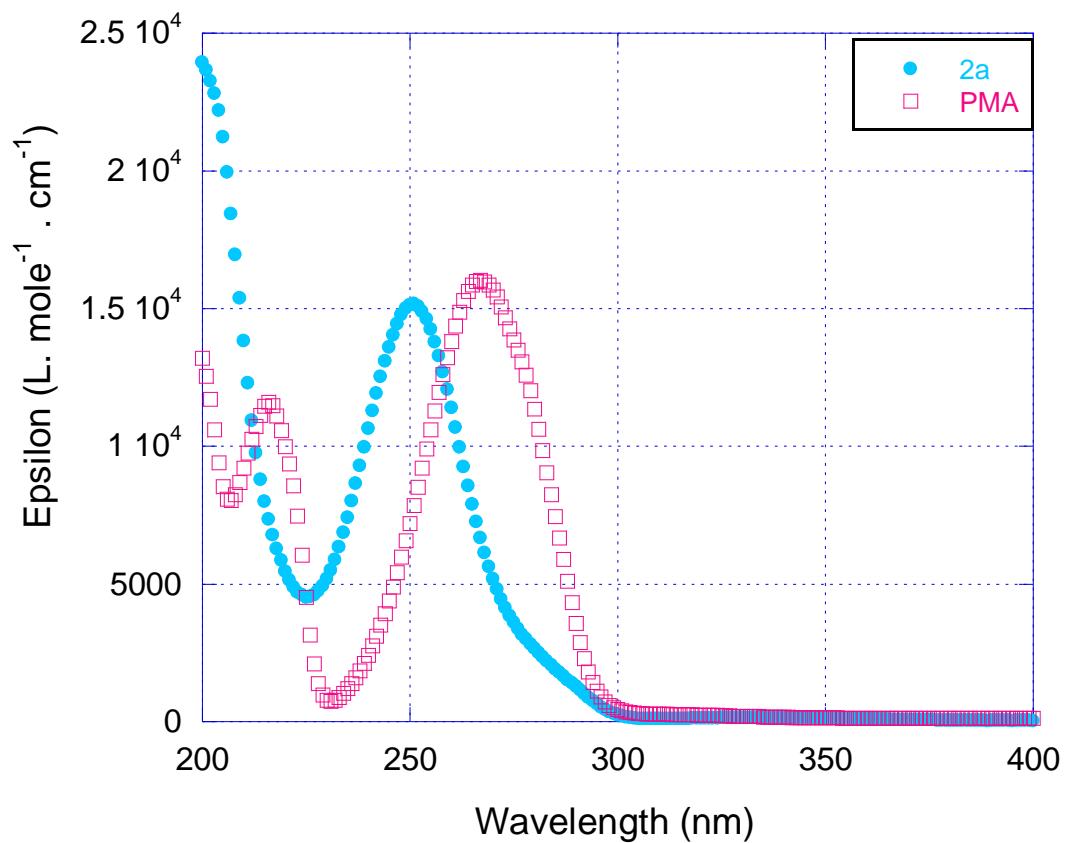


Figure S16. UV absorption spectra of S-(3-Phenylpropyl) dibenzothiophenium tetrafluoroborate (2a) and *p*-Methoxyacetophenone (PMA).

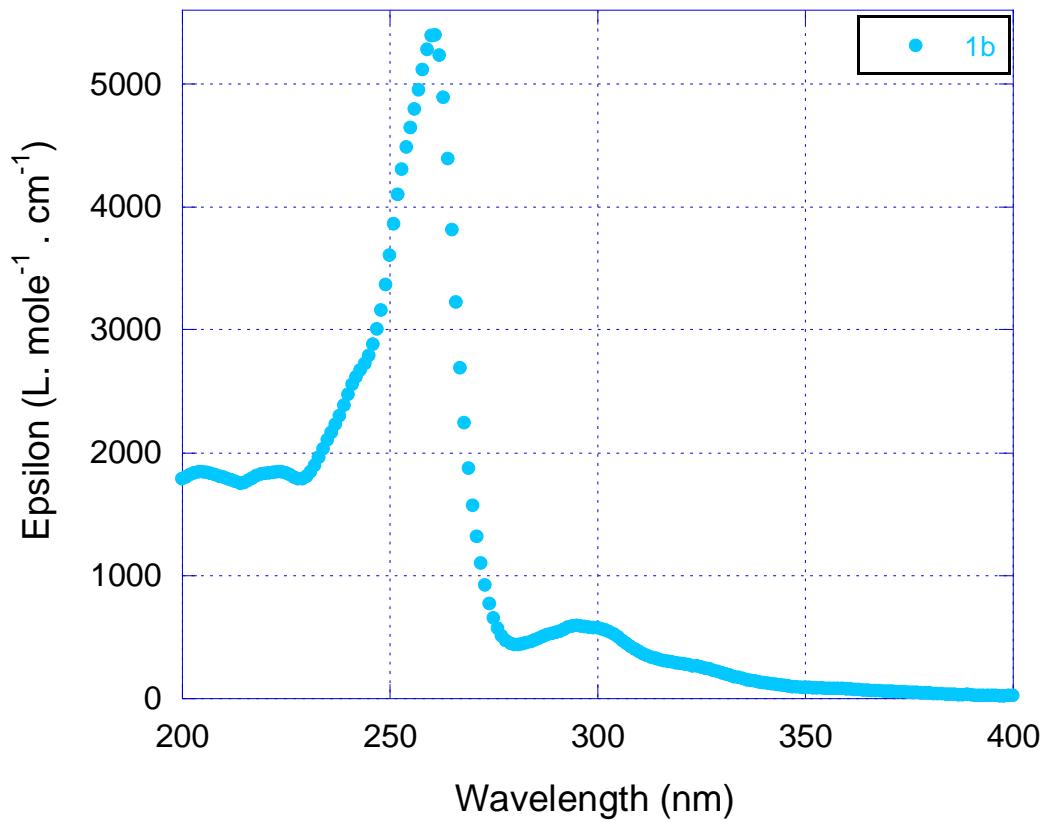


Figure S17. UV absorption spectra of S-Ethoxy 2,8-dibromodibenzothiophenium tetrafluoroborate (1b).

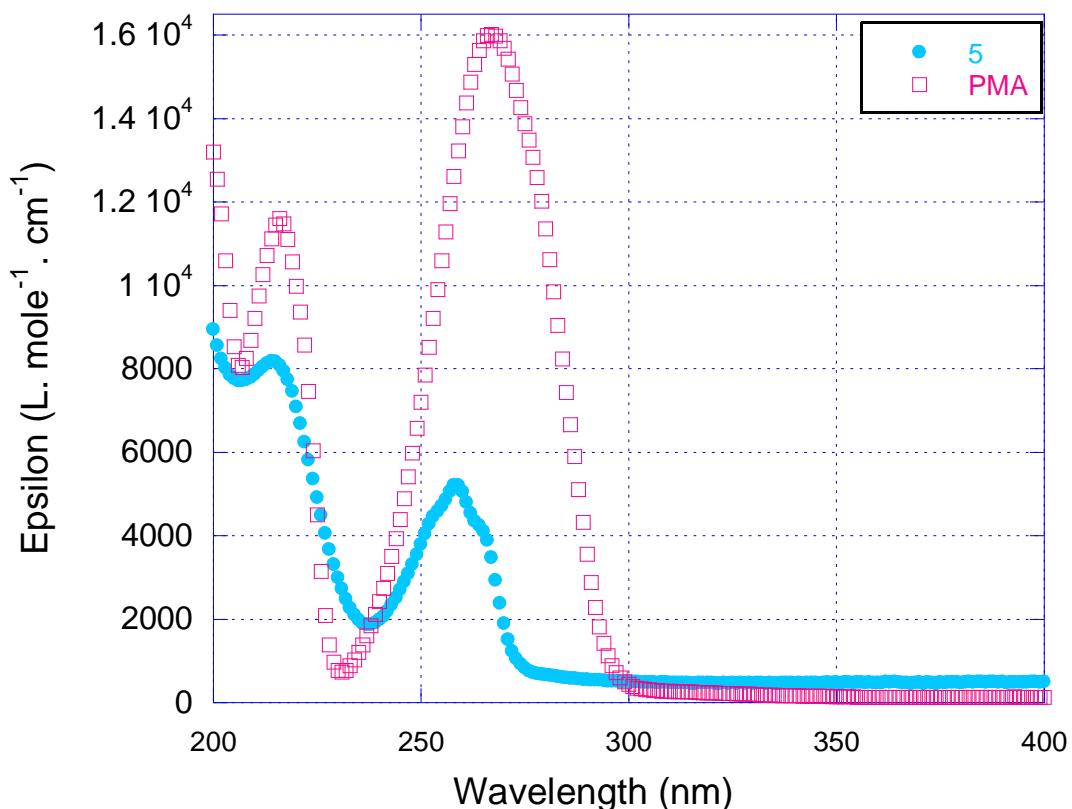


Figure S17. UV absorption spectra of N-t-butoxy pyridinium perchlorate (5) and *p*-Methoxyacetophenone (PMA).

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CHAPTER 4. GENERAL CONCLUSIONS

S,C-Ylides such as DBTY, DCTY, TY, BTY are found to be reliable photochemical precursors of dicarbomethoxy carbene. These precursors have the carbanion flanked in between two electron-withdrawing groups which delocalize the negative charge and thereby make them very stable and easy to handle in the laboratory. The nature of the product formed from the carbene depends on the spin multiplicity of the carbene and the trap used in the photolysis.

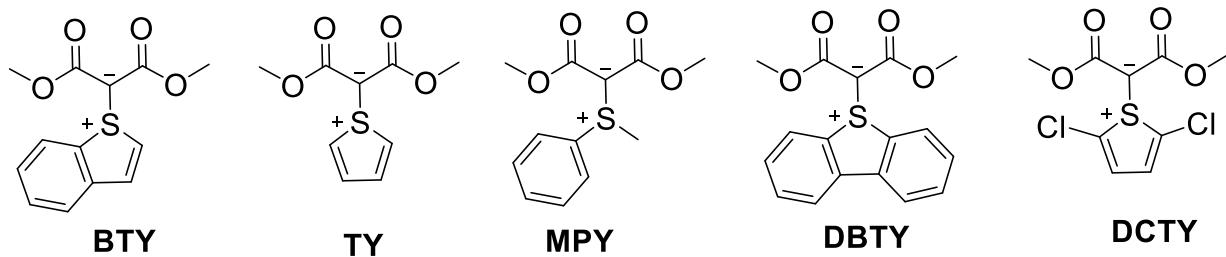


Figure 1. Structure of thiophene-S,C-ylides.

The photolysis of the DBTY and DCTY in methanol generates three products: two main products and one additional product. Singlet carbene inserts into the -OH bond of the methanol forming methoxy malonate as a singlet product, triplet carbene undergoes double hydrogen abstraction and forms dimethyl malonate as a triplet product. The third additional product is observed only in the event where oxygen is introduced (intentionally or by accident) into the reaction. The triplet carbene reacts with molecular oxygen to eventually produce dimethyl oxomalonate.

The photolysis of the DBTY and DCTY in 10% cis-4-octene in acetonitrile also generates three products: cis-cyclopropane, trans-cyclopropane, and oxazole. Singlet carbene reacts with cis-4-octene reacts in a concerted fashion with full retention of stereochemistry to form exclusively Cis-cyclopropane. Oxazole is also identified to be the product formed between

singlet carbene and the acetonitrile solvent. Triplet carbene reaction with cis-4-octene in a stepwise manner to form a mixture of cis and trans-cyclopropanes.

It was reported in our previous papers that the rate of the trapping of the initial spin population is fast compared to the ISC. Varying ratios of singlet and triplet products constant with the conversion was reported for the S,C-ylides with the exception of DBTY. The yields of the photolysis of DBTY is conversion dependent because the accumulation of DBT during the photolysis acts as a triplet sensitizer and influences the ratio of singlet and triplet products. The direct photolysis and the DBT sensitized photolysis of DBTY and DCTY in methanol and 10% cis-4-octene in acetonitrile in argon and oxygen saturation environments were reported in Chapter 2 and the phenomenon of DBT being a triplet sensitizer is well established.

S-alkoxy dibenzothiophenium tetrafluoroborates were made as potential photochemical precursors to the highly reactive alkoxy oxenium ion intermediates in parallel to the thiophene based precursors of carbenes and nitrenes we reported earlier. Photo-heterolysis is routine in these former cases but was not observed for the dibenzothiophenium salts. Instead, photo-homolysis to produce the alkoxy radical and sulfur radical cation was observed. This is in parallel to the known photochemistry of N-alkoxypyridinium compounds more than to that of sulfoxide, sulfilimines, and sulfonium ylides.

Singlet radical ion pair of the alkoxy radical and the leaving groups radical cation can undergo in-cage disproportionation, to form aldehyde and a protonated sulfur-bearing leaving group, i.e., protonated DBT, which subsequently would equilibrate with solvent. In the case of the triplet radical ion pair, radicals are expected to diffuse apart from each other in large part. An alkoxy radical generally abstracts hydrogen from the solvent to form alcohol. However, random

encounters between alkoxy radicals can result in disproportionation to form alcohol and aldehyde.

Direct photolysis and the sensitized photolysis of the salts were performed. Photolysis of the S-Ethoxy dibenzothiophenium tetrafluoroborate (**1a**) in ethanol-d₆ (a better hydrogen atom donor than the usually used acetonitrile) exclusively formed alcohol which implies the formation of the alkoxy radical. DBT radical cation was trapped as dibenzothiophene-S-oxide and the dibenzothiophene-S,S-dioxide by performing the photolysis of S-Ethoxy dibenzothiophenium tetrafluoroborate (**1a**) and S-(3-Phenylpropyl) dibenzothiophenium tetrafluoroborate (**2a**) in acetonitrile-d₃ saturated with oxygen. The data collected from the direct and sensitized photolysis strongly suggest that the precursors are undergoing photo-homolysis generating alkoxy radical and the corresponding radical cation of the leaving group.