Photochemistry of dibenzothiophene-based sulfilimines

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Photochemistry of dibenzothiophene-based sulfilimines

by

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ABSTRACT

Azides have been the most extensively investigated precursors for the photochemical generation of nitrenes. Direct spectroscopic studies as well as indirect product studies have provided adequate evidence for the intermediacy of nitrenes, in at least some azides. On the other hand, less is known on the photochemical decomposition of sulfilimines. A systematic study of the potential of sulfilimines as nitrene precursors is undertaken in the current work. 

N-Benzyol, N-acetyl, N-tosyl, N-mesyl and N-trifluoroacetyl derivatives of dibenzothiophene sulfilimine have been synthesized and analyzed for their photochemical reactivities. The extended UV-Vis absorption of the dibenzothiophene moiety allows for long wavelength photolysis and consequently provides access to a wide variety of nitrenes including the parent N-H version. The syntheses of N-H and the N-formyl derivatives of dibenzothiophene sulfilimine have also been achieved.

It has been established that benzyol and acetyl nitrenes have singlet ground states\(^1\,^2\) while tosyl nitrene has a triplet ground state.\(^3\) Our studies using time-resolved IR spectroscopy provides direct evidence for singlet and triplet nitrenes from N-benzyol and N-acetyl sulfilimine derivatives. Product studies indicate that decay via the singlet nitrene channel is the major process. N-tosyl and N-mesyl sulfilimine derivatives differ from the above two, in that, the primary decay channel is triplet nitrene capture. In the case of N-trifluoroacetyl analogue, we observed products due to both singlet and triplet nitrene intermediacy. The products observed depend on the ground state multiplicities of the corresponding nitrenes generated. Theoretical calculations were performed to estimate the singlet-triplet energy separations (\(\Delta E_{S,T}\)) for mesyl and trifluoroacetyl nitrene. Coupled-
cluster calculations predict a triplet ground state for mesylnitrene and a closely spaced singlet and triplet energies for trifluoroacetylnitrene. Hence, we observe products from both spin states in the case of trifluoroacetylnitrene while predominantly from the triplet in the case of mesylnitrene. The calculations support our inference from product studies.

All the sulfilimines analyzed indicate a potential for S-N bond cleavage from the excited triplet state of the sulfilimine. This is in line with our proposed mechanism for the photochemical unimolecular S-O bond cleavage of dibenzothiophene-S-oxide leading to O($^3P$).

References

CHAPTER 1

GENERAL INTRODUCTION - Photochemical Generation of Nitrenes

1.1 Dissertation Organization

This dissertation consists of four chapters. Chapter 1 is a literature review of nitrenes generated photolytically from azides and sulfilimines. Chapters 2 and 3 discuss the photochemistry of dibenzothiophene-based sulfilimines as potential precursors to nitrenes. All time-resolved IR measurements in Chapters 2 and 3 were performed at Johns Hopkins University, while the author performed the entire product studies. Chapter 2 discusses the photochemistry of $N$-benzoyl dibenzothiophene sulfilimine and Chapter 3 focuses on the photochemistry of $N$-acetyl, $N$-trifluoroacetyl, $N$-mesyl and $N$-tosyl dibenzothiophene sulfilimines. Synthetic efforts towards $N$-H and $N$-formyl derivatives of sulfilimines are also addressed in Chapter 3. Chapter 4 is a general conclusion of the previous chapters.

1.2 Objective

We have previously studied the photochemistry of dibenzothiophene-5-oxide and have provided supportive evidence for the formation of atomic oxygen, $[O (3P)]^{1-5}$ The main goal of this work is to broaden the scope of the dibenzothiophene platform in generating reactive intermediates, more specifically, in generating nitrenes. Dibenzothiophene-based sulfilimines (nitrene precursors) were synthesized for this purpose and their photochemical behaviors were examined in the subsequent chapters. The spin states, plausible mechanistic details and the reactivity pattern of the nitrenes and other reactive intermediates generated from the sulfilimines are the main topics of exploration in Chapters 2 and 3. One other
The objective of this work is to provide access to nitrenes that would otherwise require shorter wavelengths for their generation from other precursors. The sulfilimines analyzed in Chapter 3 address this topic considerably.

1.3 Nitrenes and their Photochemical Precursors

Reactive intermediates have had special attention in the field of organic photochemistry. Intermediates, which are difficult to access under thermal conditions, can be relatively easily generated, detected and studied under photochemical conditions. One such intermediate is the nitrene (represented below) and its chemistry generated from azide sources has been studied extensively in the last several decades.\textsuperscript{6-10}

\[
\begin{align*}
\text{N} & \text{–} \text{R}
\end{align*}
\]

The nitrene nitrogen possesses six valence electrons, which make it an electron-deficient species. However, if the neighboring R group on the nitrene contains a heteroatom, such as nitrogen, oxygen or sulfur, directly attached to the nitrene nitrogen, then the polarity of the nitrene is reversed and it behaves as a nucleophile.

Nitrenes, analogous to carbenes, are known to have triplet ground states, although exceptions to this rule also exist in the literature.\textsuperscript{11-14} The electronic structure of the parent nitrene can be easily understood by elementary molecular orbital analysis. Figure 1 depicts the MO diagram of the simplest nitrene, imidogen. Of the six valence electrons on NH, two are involved in the $\sigma$-bonding with the hydrogen (2$\sigma$) and two constitute the lone pair on nitrogen (3$\sigma$). The remaining two electrons are singly occupied in each of the degenerate non-bonding $\pi$-MOs arising from the 2$p_x$ and 2$p_y$ AO on nitrogen. Pauli’s exclusion
principle prevents the two electrons from being paired up in the same orbital and hence the ground state configuration of the nitrene is a triplet.

![Molecular orbitals of imidogen (NH)](image)

**Figure 1.** Molecular orbitals of imidogen (NH)

The triplet constitutes the lowest electronic configuration, $^3\Sigma^-$, while the $^1\Delta$ and $^1\Sigma^+$ are the two immediate higher lying electronic states as indicated in Figure 2. The energy differences measured between the states have been determined spectroscopically.$^{15,20}$
The singlet component $^1\Delta$ is comprised of the “closed-shell” and the “open-shell” states (Figure 3a and 3b). $^1\Sigma^+$ is a higher lying singlet state where an additive linear combination of the “closed-shell” components is involved.

![Figure 2. Energies of different states of imidogen (NH)](image)

**Figure 2.** Energies of different states of imidogen (NH)

![Figure 3. Representation of a) closed-shell components of $^1\Delta$ state of :NH b) open-shell and c) one of the spin components of the lowest triplet state (adapted from ref. 9)](image)

**Figure 3.** Representation of a) closed-shell components of $^1\Delta$ state of :NH b) open-shell and c) one of the spin components of the lowest triplet state (adapted from ref. 9)
Depending on the nature of the R group replacing the hydrogen atom, the degeneracy of the $^1\Delta$ components can be lifted making either the $^1A'$ or the $^1A''$ the lowest singlet states. In the case of phenylnitrene, (R = Ph), owing to delocalization of the open-shell component with the phenyl ring, the $^1A''$ is the lowest singlet state with the triplet being the ground state. However, in the case of acetylnitrene, where R = COCH$_3$, the closed-shell state, $^1A'$, derives substantial stabilization by the N-O bonding interaction that makes it the lowest singlet state, as well as the ground state of the nitrene. Details of the calculations will be discussed later in this chapter (cf. 1.3.1.2).

Singlet nitrene is relatively more reactive than its triplet analogue.$^{11-13}$ Closed-shell singlet nitrene behaves more as an electrophile and its reactivity pattern differs markedly from triplet nitrene, which is known to behave as a diradical.$^{21}$ Extending Skell’s model$^{22}$ for carbene to nitrene, we can infer singlet reactivity by its stereospecific addition to a double bond and triplet reactivity by its stepwise addition to the double bond.

**Scheme 1.** Skell’s model for carbenes adapted for nitrene addition to olefins
This difference in the reactivity pattern manifests itself in the formation of different products depending on the spin state of the reacting nitrene. Indirect product study experiments rely on the nature of the products and their distribution in order to determine the spin state of the reactive nitrene. Recent advances in laser flash photolysis with time-resolved IR techniques, transient UV-Vis measurements, along with high-level computations have provided a means to observe nitrenes, and in a number of cases, to determine their lifetimes and multiplicities directly.\(^\text{23-36}\)

A vast majority of the nitrene literature that has appeared in the last four decades focussed on azide photochemistry, with only a few reports on sulfilimines\(^\text{37-44}\) and iminopyridinium ylides.\(^\text{45}\) Deoxygenation of nitro and nitroso compounds have also been reported to give nitrene-derived products.\(^\text{46}\) However, in line with the current work, only azides and sulfilimines will be reviewed in detail.

Azide precursors commonly use the azide moiety as the primary chromophore for the absorption of light. Shorter wavelengths, such as 254 nm, have been used predominantly for direct photo excitation. Some solvents absorb at 254 nm, making them incompatible for use in photolysis. Another common disadvantage of using azide precursors is the level of caution necessary when handling them in the laboratory. Besides being highly toxic, reports of their explosive nature are also found in the literature.\(^\text{47}\) On the other hand, sulfilimines, particularly the dibenzothiophene-based ones, offer several advantages over azides. Sulfilimines are relatively safe to handle as compared to azides. The dibenzothiophene unit in the sulfilimine is the main chromophore and its absorption at relatively longer wavelengths makes it suitable for generating a variety of nitrenes. The higher quantum yield for S-N bond cleavage upon photolysis\(^\text{48}\) suggests a higher efficiency in generating reactive intermediates.
However, the syntheses of a few sulfilimines do present some challenges and these issues will be addressed in the later chapters.

1.3.1 Photochemical Generation of Nitrenes from Azides

Azide precursors to nitrenes have been the most investigated in the literature. A variety of nitrenes namely, aroylnitrenes (benzoyl, naphthoylnitrene), acylnitrenes (acetyl, ethoxycarbonylnitrene), sulfonylnitrenes (p-toluenesulfonylnitrene, methanesulfonylnitrene, benzenesulfonylnitrene, fluoroderivatives of methanesulfonylnitrene), arylnitrenes (phenylnitrenes and halogensubstititued derivatives of phenylnitrene), heteroarylnitrenes, alkynitrenes and the parent unsubstituted nitrene have been generated from azide sources. However, in line with the current work on the reactive intermediates generated from the photolysis of dibenzothiophene-based sulfilimine derivatives, the photochemistry of aroyl, acyl and sulfonyle azides will be reviewed in detail.

1.3.1.1 Photochemistry of aroyl azides

Horner and Coworkers were among the first to report the photochemical cleavage of benzoyl azide. Several reviews have appeared in the literature since then and the primary reactive species in the photochemical extrusion of N\textsubscript{2} from benzoyl azide was thought to involve the singlet nitrene. The formation of isocyanate as a side product was unavoidable and it was believed to arise from a competing reaction from the excited singlet state of the benzoyl azide (photo-Curtius rearrangement) rather than from a rearrangement of the singlet benzoylnitrene. Even in the presence of efficient traps for singlet nitrene, the yield of
isocyanate remained unaffected thereby suggesting that the singlet nitrene does not rearrange thermally to the isocyanate.43,49

![Scheme 2. Photolysis of benzoyl azide](image)

Although no direct evidence for the existence of nitrenes was available at that time, indirect product studies were suggestive of only a minor contribution from triplet nitrene. The singlet nitrene, being a powerful electrophile, was capable of inserting readily into olefins to form stereospecific aziridines, and with alcohols and alkanes to form O-H and C-H inserted products respectively. Although the reaction of singlet nitrene with olefins is expected, an alternative mechanism, where the excited state reacts with the olefin to give the same product, could not be ruled out (Scheme 3). The experimental results were interpreted assuming a triplet ground state for benzoylnitrene and a highly reactive singlet benzoylnitrene.
It had long been known that nitrenes were ground state triplets and the paradigm-shift to a possible singlet ground state was invoked by the pioneering work of Schuster and coworkers in the early 80s.\textsuperscript{11} Wasserman \textit{et al.} had previously studied ESR spectra of various nitrenes with a triplet ground state but failed to observe one for triplet benzoylnitrene upon photolysis of benzoyl azide at cryogenic temperatures.\textsuperscript{50-52} The lack of EPR observation of triplet benzoylnitrene and the formation of exiguous triplet nitrene derived products, even upon sensitization,\textsuperscript{53,54} prompted Schuster and coworkers to reinvestigate the photolysis of aroyl azide. The extended UV-absorption of naphthoyl chromophore over the phenyl analogue, facilitated the use of the former for laser transient absorption experiments and hence naphthoyl azide was chosen for detailed investigations.
The failure to detect triplet naphthoylnitrene in optical absorption experiments and in ESR studies along with the exclusive formation of singlet nitrone derived-products from sensitization experiments, enabled them to provide circumstantial evidence for a singlet ground state for aroylnitrenes. In addition to the singlet ground state, wavelength-dependant photochemistry on 4-acetylbenzoyl azide provided adequate evidence for the formation of isocyanate from a higher excited singlet state of the azide rather than the first excited singlet state.\textsuperscript{13} The authors used perturbation of the frontier orbitals in order to explain the extra stabilization of the singlet nitrene that makes it the ground state.

Subsequently, theoretical predictions using B3LYP calculations by Gritsan and Pritchina\textsuperscript{55} testified for the extra stabilization of the $^1A'$ state of the singlet benzoylnitrene relative to the $^3A''$ state of the triplet nitrene by means of a N-O bonding interaction leading to a cyclic oxazirine structure (Figure 4).

![Figure 4. Structure of singlet benzoylnitrene](image)

The singlet ground state was further confirmed experimentally using matrix isolation techniques and time-resolved IR measurements on singlet benzoylnitrene.\textsuperscript{56} Photolysis of benzoyl azide in Ar matrix at 12 K lead to the formation of two species namely, phenyl isocyanate (characterized by its calculated IR spectrum), and singlet benzoylnitrene, which was assigned based on its calculated IR and UV spectra.
High level calculations using CCSD(T) with a complete basis set extrapolation predicts a $\Delta E_{S-T}$ of -0.72 kcal mole$^{-1}$ for formylnitrene$^{56}$. As the energy separation is relatively invariant to the nature of R group on the carbonylnitrene, benzoylnitrene is also expected to follow the trend with a singlet ground state. Additional theoretical studies on acetylnitrene were performed which indicate singlet ground state for aroyl azides in general. (cf. 1.3.1.2)

Although singlet benzoylnitrene has a structure that is intermediate between a nitrene and an oxazirine, its reactivity pattern is typical of normal singlet nitrene reactivity. This has been verified experimentally and computationally by calculating the barrier heights of the reaction of benzoylnitrene with alkenes and alkanes.$^{14,57}$ Calculations predict a very early transition state for benzoylnitrene addition to an alkene with a barrier height of $\sim$3 kcal/mol. From kinetic studies,$^{14}$ the barrier height for benzoylnitrene addition to 1-hexene was calculated experimentally and the value corroborated with that obtained from theory. The low barrier height implies that singlet benzoylnitrene is a highly reactive intermediate.

Quite recently, Wentrup and Bornemann revisited the photochemistry of benzoyl azide and provided evidence for the formation of phenyl cyanate along with phenyl isocyanate.$^{58}$ Although they do not unambiguously assign the phenyl cyanate as arising from either the secondary photolysis of benzoylnitrene or directly from the excited state of the azide, nevertheless, by means of IR spectroscopy they were able to identify its presence for the first time in the photolysis of benzoyl azide.
Scheme 4. Formation of phenyl cyanate from photolysis of benzoyl azide in Ar matrix at 12K at 308 nm.

While the initial efforts to generate singlet benzoylnitrene were primarily useful for photo labeling methods, Abraham and coworkers examined the stereo electronic factors that control the potential of acylnitrenes to undergo 1,3-dipolar cycloadditions. The regiospecificity of the cycloaddition reaction appears to be entirely dependant on the nature of the double bond as evidenced by the products derived from the nitrene additions (Scheme- 5).

Scheme 5. Stereoelectronic effects of the olefin influencing the resiospecificity of the cycloaddition reactions with singlet benzoylnitrene
1.3.1.2 Photochemistry of acetyl azides

Acetyl azide photochemistry does not greatly differ from the benzoyl counterpart but further applications of acyl azide photochemistry in synthesizing complex natural products and heterocyclic rings have been explored. The laboratory convenience and the extended UV absorption of benzoyl azide make it a relatively easier candidate for detailed experimental studies. However, with regard to studies in the theoretical framework, acetyl nitrene and the corresponding azide provide a convenient molecule to model the photochemistry of acyl azides in general. Liu and coworkers compared the chemical and reactivity differences between acetyl and methoxycarbonylnitrene. (Figure 5)

![Figure 5. Acetylnitrene and methoxycarbonylnitrene](image)

DFT, CCSD(T) and CBS-QB3 methods were employed to predict the singlet-triplet energy gap of the above-illustrated nitrenes. Calculation with CBS-QB3 was more reliable as it rightly predicted a singlet ground state for acetylnitrene with the singlet state 4.0 kcal/mol below the triplet. Using isodesmic reactions, the authors arrived at the conclusion that oxygen has a stabilizing effect on both the singlet and triplet states of methoxycarbonylnitrene, but the triplet state is relatively more stabilized than the singlet state making methoxycarbonylnitrene a ground state triplet species. Their work lends further support to the work by Pritchina and coworkers on the N-O bonding interaction that stabilizes singlet benzoylnitrene.
1.3.1.3 Photochemistry of sulfonyl azides

Thermal reactions of sulfonyl azides are well preceded in the literature.\textsuperscript{64} There appears to be less doubt on the involvement of singlet sulfonylnitrene based on kinetic analysis of the thermal decomposition of sulfonyl azides.\textsuperscript{64} However, under photochemical conditions, sulfonyl azides present a rich and complex chemistry. A direct inference of the singlet sulfonylnitrene is complicated by the interference of excited state reactions of the azide, which also lead to products attributable to singlet sulfonylnitrene. Sulfonyl azides were long referred to as “starr” azides by Curtius \textit{et al.} due to their inability to undergo photo-Curtius rearrangement.\textsuperscript{65-67} However, Lwowski and coworkers have gathered evidence for such a rearrangement in the case of benzenesulfonyl azide in MeOH and they attribute product \textbf{1d} to the photo-Curtius rearrangement\textsuperscript{68} (Scheme 6).

![Scheme 6. Photochemistry of benzenesulfonyl azide in methanol](image-url)
Lwowski and coworkers were among the first to examine thoroughly the products from the photolysis of benzenesulfonyl azide in MeOH. Although Horner et al reported the possible involvement of singlet sulfonyl nitrene in the photochemistry of tosyl azide in methanol,\textsuperscript{37} the reaction appeared to be more complex. A protonation step in the excited state could lead to potentially the same product as the singlet nitrene. (Scheme 7).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme7.png}
\caption{Scheme 7. Excited state decomposition of sulfonyl azide}
\end{figure}

Also, the formation of tars when aromatics or hydrocarbons were used as solvents, made sulfonyl azides only an occasionally useful reagent for the photo-generation of singlet sulfonylnitrene.

The ability of singlet sulfonylnitrenes to insert into C-H bonds has been successfully applied in the cross-linking of hydrocarbon polymers\textsuperscript{64} such as acrylic polymers, poly(vinyl chloride), poly(vinyl ethers) etc. Numerous efforts to find efficient sources for singlet sulfonylnitrene were therefore undertaken. Abramovitch and coworkers explored a series of precursors for singlet sulfonylnitrene but found little scope for precursors other than azides.\textsuperscript{69} They performed detailed investigations on the thermolysis and photolysis of sulfonylazides.
in nonpolar, nonprotic solvents such as benzene. In the case of methanesulfonyl azide, along with the formation of unidentifiable tars, a very low yield of the azepine, 2a (from insertion into the benzene ring) was isolated.

\[
\text{SO}_2N_3 \xrightarrow{hv} \text{N} \cdot \text{SO}_2\text{CH}_3 + \text{UNIDENTIFIABLE TAR}
\]

**Scheme 8.** Photolysis of methanesulfonyl azide in benzene

The formation of azepine was mostly attributed to the involvement of singlet sulfonylnitrene. Abramovitch and coworkers found further evidence for singlet sulfonyl nitrene in their work on the photolysis of 2-biarylsulfonylazides, 3. As sulfides have been known as efficient traps for singlet nitrenes, they performed photolysis of 3 in cyclohexane containing di-tert-butyl sulfide. The major product isolated was 3c along with 3b, sultam 3a and a tan colored polymer.

\[
\text{t-Bu}_2\text{S in cyclohexane} \xrightarrow{hv} 300 \text{ nm} \quad 3a (3\%) + 3b (4\%) + (3c (20\%)) + \text{polymers}
\]

**Scheme 9.** Photolysis of 2-biarylsulfonyl azide

Although the formation of sultam 3a suggests the involvement of a singlet nitrene, the major pathway is presumed to involve ArSO$_2$⋅ radicals. The search for efficient production of singlet sulfonyl nitrene was ongoing and the difficulties in characterizing products in non
polar were resolved by performing photolyses at low conversions. Taking advantage of HPLC technique for separation, Hoyle and coworkers were able to characterize and quantify the products from the photolysis of $p$-toluenesulfonyl azide in cyclohexane and in $p$-xylene. In aromatic solvents, the authors proposed the formation of an intermediate compound, 4e, (Scheme 11), which decomposed to either product 4a or 4c.

Scheme 10. Photolysis of tosyl azide in cyclohexane and $p$-xylene

Scheme 11. Proposed mechanism for photolysis of 4 in $p$-xylene
All attempts to trap intermediate 4e by Diels-Alder chemistry were unsuccessful and this failure was attributed to a faster intramolecular rearrangement/cleavage of the intermediate 4e (Scheme 11). The mechanism proposed in Scheme 11 is similar to the one proposed by Abramovitch on the thermal decomposition of methanesulfonyl azide in benzene.\textsuperscript{74}

Most products were accounted for in the direct photolysis of arenesulfonyl azides and a plausible mechanism was invoked to account for their formation. However, the utility of sulfonyl azides under photochemical conditions is limited by the unwanted polymerizations in aromatic solvents.

Sensitized photolysis, by passing the singlet state, was examined in detail in alcohol and hydrocarbon solvents.\textsuperscript{75,76} Reagon and Nickon\textsuperscript{75} found that a radical-chain mechanism is involved in the case of direct (253.7 nm) and benzophenone sensitized (366 nm) photolysis of methanesulfonyl azide in isopropanol, where quantitative sulfonamide was obtained.

\begin{equation}
\begin{array}{c}
\text{H}_3\text{C} = \text{SO}_2 \cdot \text{N}_3 + \text{H}_3\text{C} \cdot \text{OH} \cdot \text{CH}_3 \xrightarrow{\text{hv}} 253.7 \text{ nm} \rightarrow \text{H}_3\text{C} \cdot \text{SO}_2 \cdot \text{NH}_2 + \text{H}_3\text{C} = \text{O} \cdot \text{CH}_3 + \text{N}_2
\end{array}
\end{equation}

\textbf{Scheme 12.} Direct photolysis of methanesulfonyl azide in isopropanol

Direct photolysis was auto-sensitized by acetone (formed from isopropanol), which absorbs at the same wavelength as the azide. Sensitization experiments using benzophenone in isopropanol, is often complicated by the interference of radicals generated from benzophenone and isopropanol.\textsuperscript{11,37} Therefore the formation of a “free” triplet nitrene cannot be easily interpreted under both direct and sensitized photolysis in isopropanol. Torimoto and coworkers\textsuperscript{76} explored hydrocarbons as alternatives to alcohols, and performed direct and
acetophenone-sensitized photolysis. The direct photolysis of methanesulfonyl azide in 2-methylbutane gave rise to four C-H insertion products resulting from the attack on all the primary, secondary and tertiary C-H bonds. However, acetophenone-sensitized photolysis gave rise to a different selectivity, with only tertiary and secondary C-H insertion products. C-H insertion, in the case of sulfonylnitrene, has been shown to arise from singlet nitrene rather than triplet. The formation of C-H inserted products from sensitized photolysis indicated a different mechanism not involving either the singlet or the triplet nitrene. Similar results were obtained in the sensitized photolysis in the presence of cis- or trans-1,4-dimethylcyclohexane, wherein a non-stereospecific C-H insertion was observed. Considering that singlet nitrenes would add stereospecifically to C-H bonds, and triplet nitrenes would not add, it is possible to conceive a “non-nitrene” intermediate that would account for the observed products. The triplet excited state of the azide undergoing radical mediated C-H insertion appeared the most economical interpretation for the difference in the insertion selectivities.

Several acyl and aryl nitrenes have been studied by direct spectroscopic techniques. However, the analogous sulfonylnitrene have had significantly less precedence. The complications from excited state chemistry leading to tars and polymers made sulfonyl azides less attractive for detailed kinetic experiments.

Chapter 3 discusses sulfonylnitrenes as generated from sulfilimine precursors. Although, direct observation of the nitrene has not yet been accomplished, the product studies are highly suggestive of the intermediacy of triplet nitrene intermediate. Sulfilimines appear to be viable candidates for spectroscopic studies than azides and the photolysis
proceeds more cleanly than the azide counterpart. Further details of the results will be discussed in Chapter 3.

1.3.2 Sulfilimines

1.3.2.1 Nomenclature and general properties

Sulfilimine is a more recently coined term for what was referred to as sulfimide or iminosulfurane in the older literature. The general nomenclature of sulfilimines begins with naming the substituent on the nitrogen, followed by the substituents on the sulfur atom. Sulfilimines, along with sulfoxides and sulfones, form a general class of tricoordinate organosulfur compounds. They are usually represented as shown in Figure 6a or alternatively using the semi polar bond as in Figure 6b. Although structure in Figure 6c is common for sulfoxides, the analogous sulfilimine structure raised several controversies about the true nature of the S-N linkage.

**Figure 6.** Representation of tricoordinate organosulfur compounds

The S-N bond in sulfilimine was originally considered to be a double bond and geometric isomers for the molecule were proposed\(^8\) (Figure 7).
However, such geometric isomers have never been isolated to date and low temperature (below -40 °C) $^1$H-NMR experiments on N-$p$-tosyl dimethylsulfilimine does not split the signal due to the CH$_3$ protons. This indicates that either only one structure exists or the isomers are poorly separated.$^{83}$ Later, Kuscman, examined a number of sulfilimines by x-ray crystallographic analysis$^{84}$ and proposed a $d\pi-p\pi$ overlap for the S-N linkage. His model comprised of the sulfur atom in a tetrahedral geometry and the lone pair on the sulfur being regarded as a phantom ligand. Their results indicated that the S-N linkage is not a true double bond and that the S-N bond length varied depending on the nature of the substituent on the nitrogen atom. The true nature of the S-N bond was later proved by x-ray photoelectron spectroscopy.$^{85,86}$ Tsuchiya et al.$^{86}$ compared the N-1s and S-2p binding energies of sulfilimines and their corresponding amides and aminimides. Table 1 highlights the key results relevant to discerning the nature of the S-N linkage.
Table 1. Binding Energies in eV of N-1s and S-2p in Sulfilimines and Related Compounds

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sulfilimines and Related Compounds</th>
<th>N-1s</th>
<th>S-2p</th>
<th>IR (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NH₂</td>
<td>N</td>
<td>SO₂ν(C=O)</td>
</tr>
<tr>
<td>1</td>
<td>(CH₂C₆H₄NO₂-p)(CH₃)₂N⁺NOC₆H₄NO₂-p</td>
<td>397.6</td>
<td></td>
<td>1580</td>
</tr>
<tr>
<td>2</td>
<td>H₂NCO₆H₄NO₂-p</td>
<td></td>
<td>398.7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>H₂NSO₂C₆H₄NO₂-p</td>
<td></td>
<td>399.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(CH₃)₂SNCOC₆H₄NO₂-p</td>
<td>397.2</td>
<td>164.6</td>
<td>1570</td>
</tr>
<tr>
<td>5</td>
<td>(CH₃)₂SNSO₂C₆H₄NO₂-p</td>
<td>397.5</td>
<td>166.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(CH₃)₂S(O)NSO₂C₆H₄CH₃-p</td>
<td></td>
<td></td>
<td>165.0</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>167.2</td>
</tr>
</tbody>
</table>

The binding energy of N-1s in aminimide (entry 1) is comparable to that in sulfilimines (entries 4 and 5) indicating that the N of S-N linkage is similar to the N⁻ linkage in aminimides. The N-1s binding energies in sulfilimines were lower than those in the corresponding amides (entries 2 and 3), which further validates the increased electron density on the sulfilimine nitrogen. The stabilization of the negative charge on the nitrogen by the adjacent carbonyl is indicated by the lower stretching frequency of the carbonyl. The N-N bond in aminimides is a single bond (as opposed to a partial double bond), as nitrogen cannot provide a dπ-pπ type of stabilization. Sulfilimines also show a similar stretching frequency for the carbonyl (compare entry 4 with 1), which substantiates that the S-N bond in sulfilimines is similar to the N-N bond in aminimides. Therefore the structure shown in
Figure 6a or 6b appears to be the best representation for the sulfilimine. For purposes of uniformity, the structure in Figure 6a will be utilized throughout the text.

It is conceivable from Figure 6a that if the R groups on the sulfur are different, then chiral sulfoxides and sulfilimines should be possible.

![Chemical structure](image)

**Figure 8.** Representation of chiral sulfoxides and chiral sulfilimines

Several chiral sulfoxides have been isolated and mechanistic aspects of the photo stereomutation of chiral sulfoxides have been explored. Chiral sulfilimines have also been isolated, but the corresponding photochemical influence on the racemization of chiral sulfilimines is yet to be explored.

### 1.3.2.2 Photochemical Generation of Nitrenes

Sulfilimines have not been widely used as precursors to nitrenes and only a limited number of reports on the photo labile nature of sulfilimines have appeared until the late 90s. Singlet nitrene addition to sulfides leads to the formation of sulfilimines, although a plethora of other ways to synthesize sulfilimines are also available. Horner and Christmann were pioneers in the use of sulfides and sulfoxides to trap singlet nitrenes in the form of sulfilimines and sulfoximines respectively. The reverse reaction, photochemical degradation of the sulfilimine back to the sulfide and the nitrene, was explored by Moffat *et al.* followed by Swern *et al.* which opened a gateway to novel nitrene precursors. Acetylnitrene,
benzoylnitrene, ethoxycarbonylnitrene and \( p \)-toluenesulfonylnitrene have been generated photochemically from a variety of sulfilimine platforms. In line with the current work on the dibenzothiophene platform, the chemistry of acyl and sulfonylnitrene will be discussed in detail.

### 1.3.2.2a Photochemistry of \( N \)-acylsulfilimines

\( N \)-benzoyl, \( N \)-acetyl and \( N \)-ethoxycarbonyl sulfilimines were the earliest investigated for their photochemical decomposition. Both dialkyl and diaryl derivatives of sulfilimine have been explored.

![Figure 9.](image)

**Figure 9.** a) \( N \)-benzoyl-S,S-diphenyl sulfilimine and b) \( N \)-benzoyl-S,S-dimethyl sulfilimine

The primary chromophore in all S,S-dialkyl sulfilimines is the substituent on the nitrogen and this limits the photochemical applications of the sulfilimine. In spite of this drawback, reports on the photochemistry of \( N \)-benzoyl-S,S-dimethyl sulfilimine have appeared. In cyclohexene,\(^{43}\) the sulfilimine gave rise to tars along with \( \sim 28\% \) of the aziridine, while in cyclohexane, no isolable C-H inserted product was obtained (Scheme 13). This is in contrast to the photolysis of benzoyl azide, in that 64\% of the aziridine was formed in cyclohexene and 19\% of C-H inserted product in cyclohexane.
Scheme 13. Photolysis of N-benzoyl-S,S-dimethyl sulfilimine

A comparable yield of phenyl isocyanate was formed from benzoyl azide and the sulfilimine photolysis, which lead to a reasonable conclusion of the non-involvement of singlet benzoylnitrene in the formation of phenyl isocyanate. The results by Schuster and others confirm this observation.\textsuperscript{11,13} Although singlet benzoylnitrene reactivity was evident from the sulfilimine precursor, in comparison with benzoyl azide, the latter proved to be a more reliable and efficient source for singlet benzoylnitrene.

N-benzoyl-S,S-diaryl sulfilimine did not seem attractive as it gave rise to almost a similar yield of aziridine as 5.\textsuperscript{41} An added complication with this sulfilimine is the $\alpha$-cleavage leading to biphenyl and diphenyl disulfide as side products. Furukawa and coworkers tried several variations at the R group of the diaryl sulfilimine,\textsuperscript{41} but found that the formation of isocyanate was the major product with little scope for singlet benzoylnitrene. The dibenzothiophene chromophore seems particularly attractive as it avoids the above mentioned side reaction. The dibenzothiophene is inert towards further photochemical reactions and also provides a convenient handle for generating a variety of nitrenes.
Recently, adequate evidence for the generation of singlet and triplet benzoylnitrene has been published that makes it a relevant platform for further exploration.\textsuperscript{48} Chapters 2 and 3 discuss these issues in depth.

Synthesis of a variety of thiophene sulfilimines have been reported in the literature, but their photochemical behavior is yet to be systematically studied.\textsuperscript{38} Thianthrene sulfilimines have generated enormous interest due to the interesting flip-flop motion about the S-S axis in the thianthrene ring. The molecule rests in a boat conformation and thermal inversion of chiral thianthrene sulfilimines have also been reported. Fujita and coworkers have reported the photochemical behavior of several sulfilimines in the thianthrene framework and a possible involvement of a nitrene is inferred.\textsuperscript{38} Although there is a paucity of quantitative physical data, the qualitative quantum yields are suggestive of a photo labile S-N bond.

Studies on pyramidal inversions using \textit{trans-12} and \textit{cis-12} sulfilimines yielded no apparent evidence for a photochemical inversion. The studies however, were mainly directed from a
synthetic standpoint with less emphasis on the physical organic aspects of the nitrene, namely their likely sources and their spin states.

1.3.2.2b Photochemistry of N-sulfonyl sulfilimines

Limited reports on the photochemistry of sulfonyl sulfilimines have appeared in the last few decades.\textsuperscript{39,102,103} Furukawa and coworkers\textsuperscript{103} explored the photochemical reactions of \( N-p \)-tosylsulfilimine of naphthalene-1,8-dithiole and found evidence for intramolecular nitrogen transfer to form aldimines (Scheme 14).

\[
\text{Scheme 14. Photochemistry of } N-p \text{-tosylsulfilimine of naphthalene-1,8-dithiole}
\]

Intramolecular nitrogen transfer was confirmed from cross-over experiments. The intermediate was isolated and characterized by \( ^1\text{H-NMR, } ^{13}\text{C-NMR, IR and mass spectra.} \text{Morita and coworkers reported the possible intermediacy of sulfonylnitrene when } S\text{-naphthyl-}p\text{-tosulsulfimides were subjected to photo-Stevens rearrangement (Scheme 15).}\textsuperscript{102}

The mode of cleavage (Stevens rearrangement vs. nitrene formation) depended on the nature of the solvent used. In alcohol solvents, such as methanol and isopropanol, the nitrene pathway predominated and the inference was made based on the amount of tosyl amide formed (Scheme 15a). However, in less polar solvents, such as acetonitrile and methylene
chloride, the predominant pathway is the photo-Stevens rearrangement (Scheme 15b, step 1 leading to the tricoordinate nitrogen compound).

\[
\begin{align*}
(a) & \quad \text{NTs}^- \quad \text{hv} \quad (300 \text{ nm}) \quad \text{R}^1 \text{S} \quad \text{TS}^+ \quad \text{R}^2 \text{CH}_2 \text{R}^2 \\
& \quad \text{R}^1 = 2\text{-pyridyl} \quad \text{R}^2 = 1\text{-naphthyl} \\
& \quad \text{hv} \quad \text{R}^1 \text{S} \quad \text{TS}^+ \quad \text{R}^2 \text{CH}_2 \text{R}^2 \\
& \quad \text{R}^1 \text{SSR}^1 + \quad \text{R}^2 \text{CH}_2 \text{NHTs} + \quad \text{R}^2 \text{C}_2 \text{H}_4 \text{R}^2 \\
& \quad (25\%) \quad (15\%) \quad (7\%) \\
(b) & \quad \text{NTs}^- \quad \text{hv} \quad (300 \text{ nm}) \quad \text{R}^1 \text{S} \quad \text{TS}^+ \quad \text{R}^2 \text{CH}_2 \text{R}^2 \\
& \quad \text{R}^1 = 2\text{-pyridyl} \quad \text{R}^2 = 1\text{-naphthyl} \\
& \quad \text{hv} \quad \text{R}^1 \text{S} \quad \text{TS}^+ \quad \text{R}^2 \text{CH}_2 \text{R}^2 \\
& \quad \text{R}^1 \text{SSR}^1 + \quad \text{R}^2 \text{CH}_2 \text{NHTs} + \quad \text{R}^2 \text{C}_2 \text{H}_4 \text{R}^2 \\
& \quad (33\%) \quad (54\%) \quad (\text{trace\%})
\end{align*}
\]

Scheme 15. Photochemistry of N-tosyl sulfilimine

Although it is tempting to speculate a triplet nitrene formation, the reaction could also involve a higher excited triplet state and no studies were attempted to probe this further.

Sulfilimines are yet to be investigated systematically for their photochemical behavior. This dissertation provides a systematic study and adequate evidence for their photochemical decomposition to form nitrenes and other reactive intermediates.

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CHAPTER 2

Photochemistry of Sulfilimine-based Nitrene Precursors: Generation of Both Singlet and Triplet Benzoylnitrene

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2.1 Abstract

Photolysis of \( N \)-benzoyl-\( S,S \)-diphenylsulfilimine or \( N \)-benzoyl dibenzothiophene sulfilimine produces PhNCO and also benzoyl nitrene. Direct observation of the triplet nitrene, energetic differences between the singlet and triplet state of the nitrene, and oxygen quenching experiments suggest that the triplet nitrene derives from the triplet excited state of the sulfilimine precursors, rather than through equilibration of nearby singlet and triplet states of the nitrene itself. In acetonitrile, the formation of an ylide, followed by cyclization to the corresponding oxadiazole is the predominant nitrene chemistry, occurring on the timescale of a few microseconds and few tens of microseconds, respectively. Trapping experiments with substrates such as \( \text{cis} \)-4-octene suggest that reactivity of the nitrene is mainly through the singlet channel, despite a fairly small energy gap between the singlet ground state and the triplet.


2.2 Introduction

Nitrenes are reactive intermediates that display a complex and fascinating chemistry that depends intimately on their multiplicity, mode of formation, and environment.\textsuperscript{1,6} Although most nitrenes have triplet ground states by substantial margins, aroyl nitrenes generated from aroyl azides have been notable in exhibiting primarily singlet reactivity.\textsuperscript{7} For example, acyl nitrenes generated from the corresponding azide precursors have led to stereospecifically trapped products, indicative of singlet nitrene reactivity.\textsuperscript{5,7}

Theoretical calculations and matrix isolation studies on acyl nitrenes\textsuperscript{5-9} have shown that the singlet state is lower in energy than the triplet state due to an interaction between the carbonyl oxygen and the hypovalent nitrogen. The extra stabilization of the singlet $^1A'$ state, relative to the triplet $^3A''$ state, is attributed to this bonding interaction that results in a structure that is intermediate between a nitrene and an oxazirine. Recent computational studies on acetyl nitrene using the CBS-QB3 method predict the ground state to be a singlet with $\Delta E_{S-T} = -4.9$ kcal/mol.\textsuperscript{9}

Aroyl azide precursors to aroyl nitrenes are by far the most investigated; however, we believed that evidence accumulated in other investigations suggested that certain sulfilimines might also be excellent nitrene precursors. The photochemistry of dibenzothiophene–$S$-oxide (DBTO), which results in formation of dibenzothiophene, is well documented.\textsuperscript{10-16} Numerous experiments support the formation of O($^3P$) as the major mechanism, though indirectly.
(Other authors express skepticism.\textsuperscript{17,18}) Nonetheless, use of the sulfilimine as an ylide-type photochemical precursor for nitrenes seemed attractive, particularly in light of some early reports that had reached this conclusion based on product analysis using sulfilimines of dimethyl sulfide and diphenyl sulfide.\textsuperscript{19,20} The dibenzo thiophene (DBT) platform was especially attractive, because its inherent chromophore might serve as a platform for near-UV sources for a wide variety of nitrenes: carbonyl and sulfonyl, alkyl, and the parent NH, for example.

Herein, we report trapping studies and nanosecond-microsecond time-resolved infrared (TRIR) investigation of the nature of the nitrene intermediates formed from these sulfilimine-based precursors. Results using both diphenyl sulfide- and dibenzo thiophene-based sulfilimines 1 and 2 are reported, along with a comparison to benzoyl azide, 3. In particular, we report the direct observation of 4, which has not been experimentally demonstrated previously.

\begin{center}
\begin{tabular}{c c c}
\textbf{1} & \textbf{2} & \textbf{3} \\
N-benzoyl-S,S-diphenylsulfilimine & N-benzoyl-dibenzothiophene sulfilimine & benzoyl azide \\
\end{tabular}
\end{center}

\begin{center}
\textbf{4}  \\
benzoylnitrene
\end{center}

\textbf{2.3 Results}

\begin{center}
\textbf{Time-Resolved IR Studies}
\end{center}

\textbf{Direct photolysis of 1 and 2.} Upon 266 nm laser photolysis of \textit{N}-benzoyl-S,S-diphenylsulfilimine 1 and \textit{N}-benzoyl dibenzo thiophene sulfilimine 2 in acetonitrile-$d_3$
(CD$_3$CN), the TRIR difference spectra shown in Figures 1 and 2 are obtained, respectively. The relevant kinetic traces for 2 are shown in Figures 3 and 4.²¹

![Figure 1](image_url)

**Figure 1.** TRIR difference spectra (a) over 3.6 µs and (b) over 90 µs following 266 nm laser photolysis (5 ns, 2 mJ) of N-benzoyl-S,S-diphenyl sulfilimine 1 (1 mM) in argon-saturated CD$_3$CN, overlaid with bars representing B3LYP/6-31G(d) IR frequencies (scaled by 0.96) and relative intensities of singlet (red) and triplet (black) benzoylnitrene.
Figure 2. TRIR difference spectra averaged (a) over 3.6 µs and (b) over 90 µs following 266 nm laser photolysis (5 ns, 2 mJ) of 2 (1 mM) in argon-saturated CD$_3$CN, overlaid with bars representing B3LYP/6-31G(d) calculated IR frequencies (scaled by 0.96) and relative intensities of singlet (red) and triplet (black) benzoylnitrene.
Figure 3. Kinetic traces observed at (a) 1758, (b) 1635 and (c) 1485 cm$^{-1}$ following 266 nm laser photolysis (5 ns, 2 mJ) of 2 (1 mM) in argon-saturated acetonitrile-$d_3$ and at (d) 1758 cm$^{-1}$ in oxygen-saturated CD$_3$CN. The dotted curves are experimental data; the solid curves are the calculated best fit to a single exponential function.
In CD$_3$CN, following the photolysis of either precursor (Figures 1 and 2), singlet benzoylnitrene ($^1$4) is observed at 1758 cm$^{-1}$, in good agreement with the singlet nitrene band observed in the case of benzoyl azide,$^8$ and the B3LYP/6-31G(d) calculated value (scaled by 0.96) of 1748 cm$^{-1}$. The observed lifetimes for singlet benzoylnitrene are somewhat dependent on the precursors used—about 3 µs for both sulfur-based precursors and about 10 µs for benzoylazide.

From both precursors, bands attributed to the acetonitrile-$d_3$ ylide 5-$d_3$ are observed at 1635 cm$^{-1}$ and 1330 cm$^{-1}$. (This latter band overlaps with a precursor depletion band for both sulfur-based precursors, Figures 1 and 2.) These ylide bands are produced at the same rate as
the decay of the singlet nitrene (Figure 3) and correspond to previous observations using benzoyl azide as the precursor. Over longer timescales (Figure 4), the ylide bands decay at the same rate of growth of a band at 1485 cm$^{-1}$, which we assign to oxadiazole 6-$d$, in good agreement with the reported frequency of 1480 cm$^{-1}$. Note that the other IR band of 6 at 1580 cm$^{-1}$ overlaps with a precursor band. This peak is not observed with precursor 1, due to the overlap with the strong 1480 cm$^{-1}$ band of Ph$_2$S.

Although no obvious bands are observed between 1520 and 1470 cm$^{-1}$ in Figure 2, after careful kinetic studies of the same range, we do detect one species with an IR band centered of 1485 cm$^{-1}$ upon photolysis of 2 (Figure 3c). It has a similar lifetime (about 3 µs) to that of the singlet nitrene at 1758 cm$^{-1}$, but this band vanishes in the presence of oxygen. Oxygen does not shorten the lifetime of the singlet nitrene at 1758 cm$^{-1}$ (Figure 3d), but does reduce the intensity of the kinetic trace. We do not believe that this is the triplet excited state of DBT, since 266 nm laser photolysis of DBT itself does not lead to any TRIR observable signals. Thus, this 1485 cm$^{-1}$ peak is assigned to triplet benzoylnitrene, which has a calculated peak at 1497 cm$^{-1}$ (scaled by 0.96). The 1485 cm$^{-1}$ peak is not observed after photolysis of 1, due to the overlapping 1480 cm$^{-1}$ absorption of Ph$_2$S.

On photolysis of 2 in dichloromethane, the singlet benzoylnitrene peak at 1758 cm$^{-1}$ ($k_{obs} = 6.0 \times 10^5$ s$^{-1}$, Figure 5, 6a) is observed, along with a peak assigned to phenylisocyanate, which is produced faster than the time resolution of the instrument, ca. 50 ns. Thus, the precursor to phenylisocyanate is not the relaxed nitrene, but rather an excited state of 2 or an electronically or vibrationally excited nitrene. The conclusion that PhNCO is not a product downstream from the nitrene, but rather from an excited intermediate has also been reached in related systems.

7,8,25
The triplet nitrene band at 1485 cm\(^{-1}\) band is also observed (Figure 5). It decays with a time constant of 1.8 \(\times\) 10\(^6\) s\(^{-1}\). Addition of methanol hardly shortens the lifetime of the assigned triplet nitrene band, even at 300 mM (Figure 7b), while in the presence of this amount of methanol, the lifetime of the singlet nitrene has been significantly reduced (Figure 7a). However, O\(_2\) completely suppresses the observation of the triplet nitrene band. The most economical assumption is that O\(_2\) quenches the triplet excited state that leads to formation of the triplet nitrene. Potentially, O\(_2\) could also quench \(^1\)2* to form \(^3\)2* because we expect a large singlet-triplet gap for this compound, but we have no direct evidence for this. Furthermore, it is not possible to rule out entirely the possibility that the triplet nitrene is formed and then quenched very rapidly. Ground state triplet aryl nitrenes, however, react sluggishly with O\(_2\), with rate constants typically near 10\(^5\) M\(^{-1}\)s\(^{-1}\).\(^{26-30}\) In contrast, benzyloxy nitrene and triplet carbenes react with O\(_2\) at rate constants much closer to 10\(^9\) M\(^{-1}\)s\(^{-1}\), \(^{31-34}\) which is the order of magnitude required for rapid suppression of the benzoaryl nitrene in these experiments. Regardless, the absence of a kinetic effect by methanol on the triplet nitrene and the corresponding lack of a kinetic effect of O\(_2\) on the singlet nitrene makes clear that the two nitrene spin states are kinetically distinct and not rapidly equilibrating.
Figure 5. TRIR difference spectra averaged over the timescales indicated following 266 nm laser photolysis (5 ns, 2 mJ) of $N$-benzoyl dibenzothiophenesulfilimine 2 (1 mM) in argon-saturated dichloromethane (a) between 1800 and 1465 cm$^{-1}$ and (b) an enlarged view between 1520 and 1470 cm$^{-1}$, overlaid with bars representing B3LYP/6-31G(d) calculated IR frequencies (scaled by 0.96) and relative intensities of singlet (red) and triplet (black) benzoylnitrene.
Figure 6. Kinetic traces observed at (a) 1760, (b) 1488 and (c) 2265 following 266 nm laser photolysis (5 ns, 2 mJ) of \(N\)-benzoyl dibenzothiophenesulfilimine 2 (1 mM) in argon-saturated dichloromethane and at 1760 cm\(^{-1}\) in oxygen-saturated dichloromethane. The dotted curves are experimental data; the solid curves are the calculated best fit to a single exponential function.

Figure 7. The trapping reactions of nitrenes with methanol observed at (a) 1760 and (b) 1488 cm\(^{-1}\) following 266 nm laser photolysis (5 ns, 2 mJ) of \(N\)-benzoyl dibenzothiophenesulfilimine 2 (1 mM) in acetonitrile-\(d_3\). The dotted curves are experimental data; the solid curves are the calculated best fit to a single exponential function.
**Triplet sensitized photolysis of benzoyl azide.** In previous work, some of us have demonstrated that singlet nitrene could be observed by IR from direct photolysis of benzoyl azide. However, no triplet nitrene was observed. For comparison to the data from 2, then, we examined the xanthone-sensitized photochemistry of benzoyl azide, using 355 nm laser photolysis in dichloromethane and acetonitrile-\(d_3\). Typical TRIR spectra are shown as Figure 8. Kinetic traces centered at 1636, 1660 and 1475 cm\(^{-1}\) are also shown in Figures 9 and 10.
Figure 8. TRIR difference spectra averaged over the timescales indicated, following 355 nm laser photolysis (5 ns, 2 mJ) of (a) xanthone (5 mM) and (b) benzoyl azide with xanthone (20 mM : 5 mM), and (c) following 266 nm laser photolysis of benzoyl azide in argon-saturated acetonitrile-$d_3$. ($^3X^*$: triplet excited state of xanthone.), overlaid with bars representing B3LYP/6-31G(d) calculated IR frequencies (scaled by 0.96) and relative intensities of singlet (red) and triplet (black) benzoylnitrene.
Figure 9. Kinetic traces observed at (a) and (b) 1636, (c) 1660 and (d) 1475 cm$^{-1}$ following triplet sensitized photolysis (355 nm, 5 ns, 2 mJ) of benzoyl azide (20 mM, $A_{355}$ = 0) using xanthone (5 mM, $A_{355}$ = 0.3) in argon-saturated acetonitrile-$d_3$. The dotted curves are experimental data; the solid curves are the calculated best fit to a single exponential function. (TRIR flow cell path length = 0.5 mm)
Figure 10. Kinetic traces observed at (a) 2265, (b) 1660 and (c) 1690 cm⁻¹ following triplet sensitized photolysis (355 nm, 5 ns, 2 mJ) of benzoyl azide (5 mM, A₃₅₅ = 0) using xanthone (5 mM, A₃₅₅ = 0.3) in argon-saturated dichloromethane. The dotted curves are experimental data; the solid curves are the calculated best fit to a single exponential function. (TRIR flow cell path length = 0.5 mm.)

The spectrum in Figure 8a was recorded after 355 nm photolysis of xanthone (5 mM) in CD₃CN. After rapid intersystem crossing, the triplet state of xanthone (³X*) decays back to ground state with a first order rate constant of 2.8 x 10⁶ s⁻¹ (Supporting Information). The spectrum in Figure 8b was recorded after 355 nm excitation of a similar solution with 20 mM benzoyl azide added. Negative xanthone IR bands at 1616 and 1660 cm⁻¹ and positive bands centered at 1500 and 1440 cm⁻¹ are still observed; however the lifetime of ³X* is significantly reduced.³⁵ The ylide IR band at 1636 cm⁻¹ (k_growth = 3.6 x 10⁹ s⁻¹, k_decay = 3.7 x 10⁴ s⁻¹ is still
observed, and may be compared to data obtained from direct photolysis of benzoyl azide, $k_{\text{growth}} = 3.4 \times 10^6 \text{s}^{-1}$ and $k_{\text{decay}} = 4.1 \times 10^4 \text{s}^{-1}$.\(^8\)

In the xanthone-sensitized experiments, the singlet benzoylnitrene signal at 1760 cm\(^{-1}\) cannot be detected because it overlaps with the residual signal from $^3\text{X}^*$. A new IR band, which decays at a rate of $9 \times 10^5 \text{s}^{-1}$, appears at about 1480 cm\(^{-1}\). This 1480 cm\(^{-1}\) band is certainly not due to singlet nitrene. DFT calculations were also performed on triplet excited state of benzoyl azide; there is not a significant IR band for triplet excited state of azide at that frequency (Supporting Information).\(^8\) The carrier of this IR band is very likely triplet benzoylnitrene, based on the B3LYP/6-31G(d) calculated value of 1497 cm\(^{-1}\) (scaled by 0.96).

In dichloromethane, the depletion band of benzoyl azide appears at 1690 cm\(^{-1}\) (Figure 10c, $k_{\text{obs}} = 3.5 \times 10^6 \text{s}^{-1}$), and the rate of depletion is the same as the decay of triplet excited state of $^3\text{X}^*$ at 2265 cm\(^{-1}\) in Figure 9a. This band was assigned based on data from xanthone-only controls. This is direct kinetic evidence for energy transfer from $^3\text{X}^*$ to benzoyl azide.\(^36\)

It had not escaped our attention that xanthone-sensitized experiments using 1 or 2 as the source of the nitrene were an attractive complement to the rest of the data, and some experiments were attempted. However, they were unfruitful, due to technical limitations regarding the necessary concentrations to achieve sufficient quenching, the solubility of the components, and the extinction coefficients at the appropriate laser lines.

**Product Studies**

The steady state photolysis of 2 was carried out under a variety of conditions, in order to correlate products with results from the TRIR studies. Initial concentrations were in the
range of 2-4 mM. The results of these experiments are shown in Table 1. Quantum yield determinations were done to low conversion (≤15%), but product mixtures were determined at nearly complete decomposition of starting material. All experiments were carried out in at least duplicate, and most in triplicate or greater. Uncertainties of 10-15% of the stated values are reasonable estimates. This presumably accounts for yields greater than 100%, relative to dibenzothiophene (DBT).

Measurement of loss of 2 was subject to much greater scatter than appearance of dibenzothiophene (DBT). In a limited number of experiments, measurements of loss of 2 and appearance of dibenzothiophene were identical within experimental error. Thus, since formation of DBT is directly related to potential formation of nitrene and the precision of data was much better, the yields shown in Table 1 are relative to formation of DBT.

In order to trap the expected phenylisocyanate (7), several photolyses were carried out in CH₃OH and i-PrOH, and the appropriate carbamates 8a and 8b were observed in modest yields (e.g., entries 1-4). The N-alkoxybenzamides 9a and 9b were taken as singlet nitrene quenching products under the same conditions, arising from OH insertion by the nitrene. No C-H insertion products were observed in methanol or i-PrOH. However, both are good hydrogen atom donors (typically thought of as a triplet reaction) and small amounts of benzamide were observed.
Table 1. Product yields on photolysis of 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>$\lambda$, nm</th>
<th>$\Phi$</th>
<th>Purge</th>
<th>Product yields (%), relative to DBT</th>
</tr>
</thead>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>CH$_3$OH&lt;sup&gt;a&lt;/sup&gt;</td>
<td>320</td>
<td>0.49</td>
<td>Ar</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$OH&lt;sup&gt;a&lt;/sup&gt;</td>
<td>320</td>
<td>0.36</td>
<td>O$_2$</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>i-PrOH&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>O$_2$</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>10% cyclohexane in CH$_3$CN&lt;sup&gt;b&lt;/sup&gt;</td>
<td>320</td>
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<td>52</td>
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<tr>
<td>6</td>
<td>50% cyclohexane in CH$_2$Cl$_2$</td>
<td>320</td>
<td>0.72</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>10% cis-octene in CH$_3$CN&lt;sup&gt;a&lt;/sup&gt;</td>
<td>320</td>
<td>0.76</td>
<td>Ar</td>
<td>9</td>
</tr>
<tr>
<td>8</td>
<td>10% trans-octene in CH$_3$CN&lt;sup&gt;a&lt;/sup&gt;</td>
<td>320</td>
<td>0.81</td>
<td>Ar</td>
<td>22</td>
</tr>
<tr>
<td>9</td>
<td>CD$_3$OD&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>350</td>
<td></td>
<td>Ar</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>i-PrOH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>350</td>
<td></td>
<td>Ar</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>50% cyclohexane in CH$_2$Cl$_2$</td>
<td>350</td>
<td>0.65</td>
<td>Ar</td>
<td>39</td>
</tr>
<tr>
<td>12</td>
<td>10% cyclohexane in CH$_3$CN&lt;sup&gt;b&lt;/sup&gt;</td>
<td>350</td>
<td>0.67</td>
<td>Ar</td>
<td>63</td>
</tr>
<tr>
<td>13</td>
<td>CH$_3$OH&lt;sup&gt;a&lt;/sup&gt;</td>
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<td></td>
<td>Ar</td>
<td>35</td>
</tr>
<tr>
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<td>355</td>
<td></td>
<td>Ar</td>
<td>35</td>
</tr>
</tbody>
</table>

<sup>a</sup>Product yields determined by H-NMR integration after complete conversion of starting material. <sup>b</sup>Product yields determined by GC-MS after complete conversion of starting material. <sup>c</sup>Methyl (a) or isopropyl (b) derivatives were observed, as appropriate. <sup>d</sup>Complete retention of stereochemistry from olefin to aziridine was observed. <sup>e</sup>Xanthone(ca. 4mM) as sensitizer.
Intentional introduction of O\(_2\) was used to attempt to quench long-lived triplet states and/or triplet nitrenes. Quantum yields of DBT formation were moderately reduced and the chemical yields of isocyanate-derived products 8 were moderately enhanced under these conditions. (Compare entries 2 and 4 to 1 and 3, respectively.)

Photolysis of 2 in neat acetonitrile provided oxadiazole 6 in 54% yield, with no other identifiable products. Addition of 10% cyclohexane provided the C-H insertion product 11 in low yield, while still maintaining a 52% yield of the cyclized ylide-derived product 6 (entry 5). The yield of 11 could be increased by raising the concentration of cyclohexane and switching from acetonitrile to CH\(_2\)Cl\(_2\), entry 6.

The degree of retention of stereochemistry in cyclopropane formation by carbenes or aziridine formation by nitrenes is a standard probe for singlet vs. triplet reactivity, in which stereospecific addition is taken as an indication of singlet reactivity.\(^{6,7,40-44}\) Addition of cis- or trans-4-octene to acetonitrile solutions in the photolysis of 2 causes a drop in the yield of the ylide product 6 and formation of the aziridines 12a and 12b, with full retention of stereochemistry, in 72 or 44% yield, respectively (entries 7 and 8). These product data do not distinguish between a direct reaction between the singlet benzylnitrene (14) and the alkene and the alternate possibilities of a reaction between the ylide 5 or 2* and the alkenes. (Since 6 is formed in the absence of acetonitrile, there is not a requirement of an acetonitrile ylide in the formation of aziridines.) However, they do rule out substantial reactivity between the triplet nitrene (14) and the alkenes. The yields of the two aziridines differ substantially, but it should be noted that an increased yield of 6 partially offsets the lower aziridine yield. While the reason for the yield differential is not obvious, it is at least consistent with the results of Autrey and Schuster, using napthoyl nitrene.\(^6\)
In parallel with the TRIR experiments, steady state photolyses were carried out using xanthone as a sensitizer (entries 9-12). Although triplet nitrene reactivity cannot be assumed, these conditions were assumed to produce $^32$ to the exclusion of $^12$, and thus produce the triplet nitrene, at least initially, on dissociation. In methanol, however, the singlet-trap product $9a$ was observed exclusively (entry 9). In $i$-PrOH, presumably a somewhat better H-atom donor, a substantial portion of benzamide (10) was observed (entry 10; however, see the Discussion). In a 50:50 mixture of cyclohexane and CH$_2$Cl$_2$, both benzamide and the C-H insertion product 11 were observed, consistent with at least some triplet reactivity.

Finally, to try to determine whether there might be different photochemistry for the $S_1$ and upper excited states of 2, photolyses were carried out with irradiation centered at 355 and 365 nm. We believed it more important to be doing red-edged excitation than to measure the quantum yield at the red edge, so these wavelengths were used, with the red edge of absorbance being at wavelengths just shorter than 350 nm (See Supporting Information). While this meant that quantum yields could not be measured and higher initial concentrations had to be used (ca. 8 mM, limited by solubility), the product ratios were reproducible and are shown in Table 1. There was a somewhat different mix of products derived from PhNCO vs. the nitrene (compare entries 13-15 to entries 1-2), but there were no new products, nor products that were excluded. This is in contrast to benzoyl azide as a precursor to benzoyl nitrene, in that the azide is thought only to produce phenylisocyanate from an upper excited state.$^7$

For comparison, direct photolysis of benzoyl azide in $i$-PrOH (compare to entry 3 of Table 1) produced 2% benzamide, 53% 8b, and 48% 9b, relative to consumed benzoyl azide. Photolysis at 350 nm of an $i$-PrOH solution containing xanthone resulted in benzamide as the
sole identifiable product, in quantitative yield. However, it has previously been demonstrated that, under similar conditions (photochemically active sensitizer, alcoholic solvents), an aroylamide is produced by a radical chain mechanism that does not derive from triplet sensitization of an aryl azide, but rather begins with hydrogen abstraction from \textit{i}-PrOH by xanthone.\textsuperscript{7,45}

2.4 Discussion

The combination of TRIR and product study results allows several conclusions to be drawn regarding the photochemistry of 1 and especially 2. The product studies focused on 2 for a few reasons. First among these is that the absorption spectrum of 2 is shifted to the red of 1. Although the presence of the sulfilimine (or sulfoxide, as in the photochemistry of dibenzothiophene sulfoxide) interrupts the extended aromaticity of DBT, the comparable chromophore is a biphenyl group, rather than isolated benzene rings, as in 1. Thus, in the long run, with nitrenes that do not have a convenient chromophore (e.g., simple alkynitrenes derived from simple N-alkylsulfilimines), the extended chromophore should be an advantage. Also, the inherent S-N bond dissociation energy of sulfilimines derived from DBT should be lower than those derived from diphenyl sulfide, because the product that is generated (i.e, dibenzothiophene) gains aromaticity, in analogy to the sulfoxide analogs.\textsuperscript{46} Finally, again appealing to the sulfoxide photochemistry analog, the photochemistry of diphenyl sulfoxide\textsuperscript{47} is known to be more complex than that of dibenzothiophene.\textsuperscript{11,48}

A comment on sulfoxide deoxygenation chemistry is also in order with the results of this paper. Although extensive \textit{indirect} evidence has existed that the mechanism is a unimolecular dissociation to form atomic oxygen O(\textsuperscript{3}P) and the sulfide, direct evidence is
lacking, due to the paucity of spectroscopic handles in solution for O(3P). The unambiguous
direct observation of nitrene formation from 1 and 2 is, of course, possible due to the nitrene
IR spectrum (and the UV/Vis absorption, though that is not discussed in this paper). Thus,
while still indirect because the molecules are not identical, we view this result as a yet
another indication that unimolecular dissociation of sulfoxides to sulfides and atomic oxygen
is a plausible and active mechanism in at least some instances.

We now focus on the detailed results presented here and their implications for the
detailed dynamics for 2 and, below, for benzoyl azide. The experiments presented here
regarding 2 present firm evidence for (1) intermediacy of both the singlet and triplet nitrene,
(2) a fast process, which is independent of the relaxed singlet nitrene, that generates
phenylisocyanate, and (3) a lack of rapid equilibration of the two spin states of the nitrene.
Particularly notable is the direct observation of the triplet nitrene.

The anticipated excited state energies for 2 are worth noting, in that they influence our
interpretation of the dynamics, which is illustrated as Scheme 1. The UV absorption
spectrum above 250 nm shows a shoulder at approximately 320 nm for its low energy
maximum (ca. 89 kcal/mol), and absorption is ended by 350 nm (ca. 82 kcal/mol). Although
the extinction coefficients vary, the positions of the first two bands are similar for 2 and
dibenzothiophene-S-oxide. We thus conclude that the photochemically accessed excited
state, is likely centered mainly on the DBT moiety. Acetophenone, however, does have a
1nπ* absorption with a low extinction coefficient (<100 M⁻¹cm⁻¹) in the same general area.⁴⁹
Our present data do not distinguish between two similar-energy excited singlet states for 2
near 85 kcal/mol and a single excited state of either mixed character or localized on the DBT
moiety.
The triplet states of 2 were not observable by phosphorescence spectroscopy at 77 K. This was not a surprise, in that dibenzothiophene-S-oxide phosphoresces very weakly.\(^{50}\) (Sulfoxidic derivatives of pyrene phosphoresce at energies very close to that of unsubstituted pyrene. See ref\(^ {51}\).) Given that any triplet n\(\pi^*\) state of 2 is expected to be within perhaps 10 kcal/mol of the corresponding singlet, we believe that \(T_1\) will most resemble dibenzothiophene-S-oxide, whose triplet energy is well-separated from its singlet (as is the case for most large arenes) and is observed at about 60 kcal/mol, depending on the solvent.\(^{50}\) These energetic considerations are reflected in Scheme 1, in which intersystem crossing from \(^12^*\) to \(^32^*\) is shown as irreversible.

As previously discussed, the timescale of formation of PhNCO (and much slower decay of the singlet nitrene) clearly demonstrates that the nitrene is not the precursor of the isocyanate. In work on related aroyl azide photochemistry, Schuster reported a wavelength

\[\text{Scheme 1. Photochemistry of 2}\]
dependence that showed that an upper excited state was the precursor to the isocyanate, in that red edge photolysis provided only nitrene-derived products. However, we find that red-edge excitation of 2 (entries 13-15, Table 1) also provides PhNCO. This eliminates the upper excited state possibility. The most economical assumption is that its precursor is the same singlet excited state that gives rise to the nitrene. Of course, we cannot rule out a more complex, very rapid pathway. (For example, Gudmundsdóttir recently demonstrated a competition between a-cleavage of a pure benzoyl chromophore and energy transfer to an azide. Here, one might imagine that a close-lying benzoyl-derived state would directly form PhNCO, while the DBT-derived state might provide the nitrene.)

The TRIR spectra in Figures 1 and 2 are in good agreement with previous reports for the formation of singlet benzoylnitrene from benzoyl azide, based on the peak at 1758 cm\(^{-1}\). The appearance of this peak is instantaneous on this timescale. The decay time constant is about the same for 1 and for 2 as precursors, about 3 \(\mu s\), which is about 3 times faster than that recorded for benzoyl azide as a precursor. An attractive interpretation is that lifetime shortening is due to trapping of the nitrene by the newly-formed sulfide. For example, it is known that dimethyl sulfide is a good quencher of \(^1\)4.52

The parent-daughter relationship between the singlet nitrene and the ylide (5) band at 1635 cm\(^{-1}\) is confirmed by the growth rate of the latter. It, in turn, shares a parent-daughter relationship through kinetic measurements with oxadiazole 6, with time constants of the order of 30 \(\mu s\). Given this sequence, the appearance and assignment of the singlet nitrene is confirmed. Furthermore, the decay rate of the singlet nitrene in dichloromethane is about six times smaller than that in acetonitrile, implying that there is an additional decay process available in the latter solvent. From the two observed decay rates (Figures 3 and 6), we infer
a rate constant for reaction between the nitrene and acetonitrile to form the ylide of approximately $1.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$.

The collection of kinetic traces show that there is not rapid interconversion between the two spin-states of the benzoyl nitrene, particularly the methanol quenching experiments reflected in Figures 6 and 7. The observed decays for singlet and triplet nitrene are similar in acetonitrile. In addition, the lack of observation of the triplet nitrene in the presence of O$_2$ could at least potentially reflect quenching of $^3\text{2}$ or $^3\text{4}$, so these data are ambiguous. However, the data in Figures 6 and 7 are not, in that the singlet is quenched by methanol while the triplet is not.

The observed products are mainly attributable to reactivity of the singlet nitrene (and PhNCO), as opposed to the triplet nitrene. The singlet nitrene is unambiguously involved in the formation of adducts $\textbf{8a}$ and $\textbf{8b}$ in alcoholic solvents, and in the formation of aziridines with full retention of stereochemistry in the presence of alkenes.

The one observed product we can most clearly attribute to triplet chemistry – at least in the case of direct irradiation – is benzamide, $\textbf{10}$, which is generally observed in only small amounts (Table 1). Previous workers have demonstrated that excited triplet aroyl azides may react with cyclohexane to give part of the yield of benzamides observed on photolysis of benzoyl azide and its analogs.$^7$ We cannot rule out some analogous reaction of $^3\text{2}$, though it seems less likely than in the case of the aroyl azides, due to the much different, and presumably DBT-centered, excited state involved.

Given the observed lifetime of the triplet nitrene, hydrogen abstraction by it from methanol or $i$-PrOH would require rate constants of the order of $\leq 10^5 \text{ M}^{-1}\text{s}^{-1}$; this does not seem out of line. Based on the lack of observation of any mixed-stereochemistry aziridine,
we must further infer that the rate constant for reaction between triplet nitrene and the simple alkene is <10^6 M^{-1}s^{-1}, assuming the first step of C-N bond formation is irreversible. This is also an expected result.\textsuperscript{7,53}

Because not all the mass balances are excellent, we considered other possible products. Gudmundsdottir has recently shown that triplet alkyl nitrenes dimerize and yield products derived from their photolytic loss of N\textsubscript{2} in a secondary reaction.\textsuperscript{54-56} The illustrated expected analog would yield benzaldehyde; no evidence of that product has been obtained.

\[
\begin{align*}
3 \left[ \text{PhN}=\text{O} \right] \quad & \quad \rightarrow \quad \text{PhN}=\text{N} \quad \text{Ph} \\
\text{hv} \quad \text{RH} \quad \rightarrow \quad \text{PhCHO}
\end{align*}
\]

However, this dimerization-based product is not strongly expected, because the alkylnitrenes Gudmundsdottir examined, in contrast to acyl nitrenes, should abstract hydrogens very slowly and are long-lived.\textsuperscript{54-57}

The insertion of the nitrene into cyclohexane is a product that can be attributed, in principle, to either singlet or triplet chemistry. Elegant experiments by Hall and coworkers explicitly argued for the partial intervention of triplet phenylnitrene in certain C-H insertions,\textsuperscript{58} though others have argued such insertions were due to singlet chemistry in cases closely related to ours.\textsuperscript{7,42} Our experiments do not clarify this further, though it was important to established the full set of expected reactivity for this novel nitrene precursor.

Although the TRIR data show that the singlet and triplet nitrenes are kinetically distinct and do not rapidly equilibrate, the IR data do not directly quantify the relative amounts of
formation of the two species, unfortunately. Neither do the product yields, because the triplet nitrene – being energetically higher than the singlet nitrene – can, in principle form singlet nitrene by “irreversible” intersystem crossing.

Despite this caveat, the product yield data on direct photolysis never show more than a few percent of products due to triplet chemistry, and the triplet nitrene signal in the TRIR experiments is weak, compared to that of the singlet nitrene. This is suggestive of a low yield of $^34$. Additionally, O$_2$ lowers the quantum yield of DBT formation (Table 1). All these data can be reconciled by assuming that a comparatively small fraction of $^12*$ partitions to $^32*$ and thus the triplet nitrene. Of this fairly small fraction of triplet nitrene, some reacts with solvent by hydrogen abstraction to yield benzamide when appropriate H-donors are available, and the rest decomposes to singlet nitrene. We assume that the comparatively small contribution that this makes to the total singlet nitrene population (and the quality of the TRIR data) make it difficult to detect this “growth” component of singlet nitrene. The oxygen quenching results are consistent with this interpretation, particularly if we allow that O$_2$ may additionally quench $^12*$ because of the large energy gap between $^12*$ and $^32*$. Addition of O$_2$ lowers the overall quantum yield of DBT formation, indicating quenching of the excited states before nitrene formation. An increase in the relative yield of PhNCO is consistent with quenching of $^32*$ specifically, because it indicates that $2*$ is “recycled” after having already losing a fraction of its population to the formation of PhNCO.

When xanthone is used as a triplet sensitizer, we presume that $^32*$ is generated specifically. According to Scheme 1, this gives exclusively the triplet nitrene. Yet entries 9 and 12 in Table 1 in particular indicate clearly singlet products: OH insertion to form 9a in methanol, and addition of acetonitrile to form 6 in 90% CH$_3$CN. This is accommodated by
the intersystem crossing of the triplet nitrene down to the singlet. We presume, but have not proved, that at least much of the 43% yield of benzamide on xanthone-sensitized photolysis of \( i\)-PrOH is due largely to the type of radical chain mechanism that leads to amide formation in aroylazide chemistry in alcoholic solvents.\(^7\) However, a somewhat faster hydrogen abstraction rate constant from \( i\)-PrOH than from methanol might also account for formation of benzamide, if it brought the rate of hydrogen abstraction to be competitive with intersystem crossing down to the singlet nitrene. Ideally, we would have TRIR data to show the rate of this growth of the singlet nitrene population at the expense of the triplet population, but these experiments proved technically infeasible.

For benzoyl azide, we reach a different conclusion regarding the excited state dynamics, as shown in Scheme 2. The singlet and triplet states of the azide are likely to be only a few kcal/mol apart, given the carbonyl’s involvement in the low energy excited state. Moreover, on sensitization with xanthone, growth of the ylide \( 5 \) is observed on a rapid timescale that is inconsistent with formation of the singlet nitrene via slow isc through the triplet nitrene. Instead, we believe, there is rapid equilibration in the excited states before nitrene formation. Because the triplet state is, presumably, of lower energy, we can infer that cleavage of \( ^1\)PhCON\(_3\) to the corresponding singlet nitrene occurs faster than in the triplet manifold.
Furthermore, because PhNCO is not produced on xanthone sensitization (as evidenced by lack of formation of 8b), we tentatively assign the precursor of the isocyanate to be an upper excited singlet, in parallel with the findings of Schuster. The quantitative chemical yield of benzamide, however, under these conditions is likely due to the type of radical chain mechanism observed by Schuster and others, rather than the intervention of quantitative hydrogen abstraction by the triplet nitrene.

2.5 Conclusions

The observation of characteristic bands in the infrared, high quantum yield of dibenzothiophene formation, and characteristic product formation all demonstrate that sulfilimine 2 is a relevant precursor to benzoylnitrene. Both singlet and triplet nitrene are observed directly. Shorter nitrene lifetimes with 1 or 2 than when benzoyl azide is used as a precursor suggest that back reaction with the sulfide may be a significant process. Triplet
benzoyl nitrene, although not the ground state of the nitrene, still disappears only on the microsecond timescale. Given the paucity of triplet-derived products, we believe the major pathway for its decomposition is relatively slow intersystem crossing to the ground state singlet. Although phenylisocyanate is a troublesome byproduct of photolysis of 2, this alternate reaction of \(^12\) is obviously dependent on the presence of the adjacent carbonyl group; thus we conclude that sulfilimines based on dibenzothiophene are likely to be useful precursors to a variety of nitrenes. Further work is underway.

2.6 Experimental Section

Time resolved IR methods. The TRIR experiments have been conducted following the method of Hamaguchi and coworkers\(^ {59,60}\) as has been described previously.\(^ {61}\) Briefly, the broadband output of a MoSi\(_2\) IR source (JASCO) is crossed with excitation pulses from either a Quantronix Q-switched Nd:YAG laser (266 nm, 90 ns, 0.4 mJ) operating at 200 Hz or a Continuum Minilite II Nd:YAG laser (266 nm, 5 ns, 2 mJ) operating at 15 Hz. Changes in IR intensity are monitored using an ac-coupled mercury/cadmium/tellurium (MCT) photovoltaic IR detector (Kolmar Technologies, KMPV11-J1/AC), amplified, digitized with a Tektronix TDS520A oscilloscope, and collected on a Macintosh with IGOR for data processing. The experiment is conducted in dispersive mode with a JASCO TRIR 1000 spectrometer.

Computational Methods Geometries were fully optimized at the respective level of theory, and all stationary points were confirmed to be energy minima by vibrational frequency analysis. The B3LYP\(^ {62-64}\) calculations were performed with Gaussian 98.\(^ {65}\)
**General steady state photolysis methods.** Solvents used were “spectral grade” and were used without further purification. The photolyses and quantum yield measurements were carried using a 75W Xenon Arc lamp (Photon Technologies Inc) fitted to a monochromator set to the specified wavelength with ± 12 nm linear dispersion. Valerophenone was used as the actinometer, and the photolysis at 320 nm to form acetophenone was monitored by HPLC. Samples were placed in a 1 cm square quartz cell mounted on a holder such that all the light emanating from the monochromator hits the sample directly (OD >2). Initial concentrations were 2 - 4 mM. Except as noted, all solutions were bubbled with Ar for at least 10 min, prior to photolysis. The progress of reactions was monitored by HPLC analysis, using an HP 1050 HPLC with a diode array UV/vis detector with a C18 reverse phase column for separation. All reported yield data represent at least duplicate experiments, and most were carried out in triplicate or greater.

Quantum yields were measured by monitoring the appearance of DBT, using HPLC detection and low conversions. Product yields reported in Table 1 were determined from runs done to nearly complete conversion. Reactions for product yield determinations were typically stopped when only a few percent of the original starting material remained. Identification and quantification were done by a combination of $^1$H NMR and GC-MS (EI, DB-5 column) of crude reaction mixtures. Products were identified by comparison of data to authentic samples for all compounds except 8b, 9b, and 12b. Compounds 8b and 9b were known in the literature, and the reported $^1$HNMR was relied upon. The $^1$H NMR spectrum of the analog of 12b made from trans-3-hexene (as opposed to trans-4-octene) and its analogy to the spectrum and GC-MS of 12a was used as evidence of structure.
Compound preparation

*N*-benzoyl-*S,S*-diphenylsulfilimine \(1^9\), benzoyl azide \(3,^70\) carbamate \(8a,^71\) *N*-methoxybenzamide \(9a,^71\) and oxadiazole \(6^72\) were prepared by literature methods. *cis*-Aziridine \(12a\) was prepared by the method of Tanner,\(^73\) previously applied to the hexene derivative, rather than the octene derivative. \(^1\)H-NMR (CDCl\(_3\)) \(\delta\) 1.01 (t, \(J = 7.2\) Hz, 6H), 1.44-1.66 (m, 6H), 1.7-1.8 (m, 2H), 2.52-2.58 (m, 2H), 7.45 (t, \(J = 7.6\) Hz, 2H), 7.55 (t, \(J = 7.6\) Hz, 1H), 7.99 (d, \(J = 7.2\) Hz, 2H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 14.0, 20.6, 30.1, 42.3, 128.3, 129.2, 132.5, 133.8, 180.4. Compounds \(8b\) and \(9b\) were identified by comparison to literature reports of their \(^1\)H NMR spectra,\(^67,68\) in addition to MS data.

*N*-benzoyl-*S,S*-dibenzothiophene sulfilimine \(2\). This compound was prepared in two ways. **Method A** was in close analogy to that of Nakayama.\(^74\) To a solution of trifluoroacetic anhydride (0.706 mL, 5.0 mmol) in CH\(_2\)Cl\(_2\) at \(-78\) °C, was added dibenzothiophene-*S*-oxide\(^11\) (0.5 g, 2.5 mmol) in CH\(_2\)Cl\(_2\). The reaction was stirred at this temperature for 30 min. At \(-60\) °C, a solution of benzamide in THF (0.606 g, 5.0 mmol) was added, and the reaction was held at this temperature for 90 min. The reaction mixture was then slowly warmed up to room temperature. The reaction mixture was washed with saturated sodium bicarbonate and the organic layer is dried and concentrated to give the crude product. Purification was by silica chromatography using 5% EtOAc in CH\(_2\)Cl\(_2\) as eluent to give \(2\) in 30% yield. \(^1\)H-NMR (CDCl\(_3\)) \(\delta\) 8.26 (d, \(J = 7.2\) Hz, 2H), 8.13 (d, \(J = 6.9\) Hz, 2H), 7.95 (d, \(J = 7.8\) Hz, 2H), 7.69 (t, \(J = 7.5\) Hz, 2H), 7.56 (t, \(J = 7.5\) Hz, 2H), 7.3-7.5 (m, 3 H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 122.3, 127.9, 128.9, 129.0, 129.9, 130.0, 131.0, 132.4, 135.9, 138.4, 138.4, 178.6. MS (m/z) 303, 274, 200, 184. IR 1592, 1545, 1333, 1292, 755, 714 cm\(^{-1}\).
Method B  

*Method B*  

*N*-p-tosyldibenzothiophene sulfilimine was made followed the known literature procedure for related compounds.\(^75\)  

*N*-p-tosyldibenzothiophene sulfilimine (1.0 g, 2.8 mmol) was dissolved in 10 mL concentrated sulfuric acid (95%) at room temperature for about 2 hours, and the resulting solution was then poured into 100 mL cold diethyl ether. After removal of the ether, the oily mixture was dissolved in 100 mL chloroform, washed with ammonium hydroxide (2 x), followed by water (5 x), dried with sodium sulfate, and the solvent was removed. The white solid was then dissolved in 50 mL benzene. To this was added in benzoic anhydride (0.65 g, 2.8 mmol). The resulting solution was allowed to stir for 1 h. Then benzene was removed, and the residue was dissolved 50 mL dichloromethane, washed with water (5 x), dried with sodium sulfate, and the solvent was removed. The residue was chromatographed on silica gel using 10% ethyl acetate/hexane as an eluent to give 0.4 g (50%) of an off-white solid.

### 2.7 Acknowledgments

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### Supporting Information

Additional TRIR data and documentation of all computational data are provided in Appendix A.
2.8 References


(21) Kinetic traces obtained with 1 are shown in the supporting information.


(24) Other DBT-based sulfilimines do not produce this peak on photolysis, implying it is not a band due in any way to DBT. Full data on other systems will be published separately.


(35) A control experiment using 20 mM benzoyl azide in the absence of any xanthone does not show any photochemistry.

(36) A band appears at this frequency on direct photolysis at 266 nm, but it does not decay on this timescale, and is assigned to PhNCO, as discussed previously.


CHAPTER 3

Photochemistry of N-Acetyl, N-Trifluoroacetyl, N-Mesyl and N-Tosyl Dibenzothiophene Sulfilimines

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3.1 Abstract

N-acetyl and N-trifluoroacetyl, N-mesyl- and N-Tosyl derivatives of dibenzothiophene sulfilimine have been studied for the generation of reactive intermediates upon photolysis. Time-resolved IR experiments provide direct evidence for singlet and triplet acetylnitrene from photolysis of N-acetyl dibenzothiophene sulfilimine. Steady-state product studies indicate decay via the singlet channel as the major pathway. N-tosyl, N-mesyl and N-trifluoroacetyl sulfilimines differ substantially from the N-acetyl derivative. N-tosyl and N-mesyl derivatives yield primarily triplet-derived products while N-trifluoroacetyl derivative yields both singlet and triplet nitrene-derived products from photolyses. Calculations using coupled-cluster methods predict that mesylnitrene is a ground state triplet while trifluoroacetylnitrene has closely spaced singlet and triplet energies. The products observed are consistent with the ground state multiplicities of the corresponding nitrenes generated.
3.2 Introduction

The chemistry of nitrenes is, if anything, more complex than that of their isoelectronic carbene cousins.\textsuperscript{1-6} For example, while only the closed shell singlet is usually relevant for carbenes, the open-shelled singlet can be an important state for nitrenes. Moreover, while the ground state for simple nitrenes is of triplet multiplicity (by tens of kcal/mol), relatively slow intersystem crossing rates and rapid reactions of the singlet often make detection of the triplet ground state difficult. In simple cases, rearranged imines, rather than nitrenes, are detected even at cryogenic temperatures.\textsuperscript{3}

$\alpha$-Ketonitrenes, such as benzoylnitrene (2a), on the other hand, have singlet ground states, due to a very strong stabilizing interaction between the oxygen lone pair and the nominally empty orbital on nitrogen. This results in a narrowing of the O-C-N angle and strong bonding interactions.

\begin{center}
\includegraphics[width=0.5\textwidth]{nitrene_diagram}
\end{center}

By contrast, although the same interaction exists for the closed-shell singlet state, alkoxy carbonylnitrenes have triplet ground states, the singlet stabilization apparently being subtly less important.\textsuperscript{3}

Despite their structural similarity to the carbonyl case, the available evidence from photolysis of tosyl azide is that toluenesulfonylnitrene (2e) has a triplet ground state, as established by the observation of a low temperature EPR signal.\textsuperscript{3,7,8} Nonetheless, the chemistry of sulfonylnitrenes is not well established because of problems with the usual sulfonylazide precursor. These have often led to difficult mixtures with hard-to-characterize precipitates.\textsuperscript{4} The excited-state or heated azides can lead to exactly the same products as the
sulfonylnitrenes. Other problems also exist. Despite the apparent triplet multiplicity of the sulfonylnitrene ground states, thermolysis or photolysis of sulfonylazides generally leads to negligible amounts of triplet-nitrene-derived products.\textsuperscript{7,9-15} Complexities deriving from the possibility of reactions of the excited states of the azide (as opposed to going through the nitrene and from the hazards associated with smaller azides (e.g., mesyl azide) have been noted.\textsuperscript{10,14,16-19} Finally, SO\textsubscript{2} extrusion is observed under some circumstances. For these reasons sulfonyl azides have been called only "occasionally useful" precursors to sulfonylnitrenes.\textsuperscript{7,20} Thus other precursors are clearly valuable in elucidating the chemistry of sulfonylnitrenes.

We recently reported the photolysis of \textit{N}-benzoyl dibenzothiophene sulfilimine \textit{1a}, which generates dibenzothiophene (DBT) and the nitrene \textit{2a}\textsuperscript{21}. Both singlet and triplet benzoylnitrene were directly observed by time-resolved infrared spectroscopy (TRIR) and confirmed by product studies. We have also recently reported product studies demonstrating the formation of carbenes from similarly derived \textit{S}-\textit{C} ylides of dimethyl malonate with thiophene derivatives.\textsuperscript{22} Nearly simultaneous with our publication regarding benzoylnitrene, Morita and coworkers reported photochemically induced \textit{S}-\textit{N} cleavage of several \textit{N}-tosyl and \textit{N}-acyl thianthrene sulfilimine derivatives.\textsuperscript{23} Intra- and intermolecular trapping of presumed nitrene intermediates by thianthrene and diphenyl sulfide was noted, in addition to formation of tosyl amide from the \textit{N}-tosyl derivatives and other reactions related to stereochemical inversion of the thianthrene derivatives.\textsuperscript{23} Much earlier, the first chemical trapping evidence of nitrene formation from sulfilimines arose from photolysis of \textit{N}-\textit{p}-tosyl dimethylsulfide sulfilimine and a few related derivatives,\textsuperscript{24-26} though in these instances, the nitrene provided the chromophore, rather than the sulfide. As a matter of principle, the use of either
thianthrene or dibenzothiophene should represent an improvement over dimethyl sulfide for the basic reason that the chromophore does not need to be tied to the nitrene being produced.

In this chapter, we present a systematic study using a set of $N$-substituted analogs of 1a designed to produce several different carbonylnitrenes and sulfonylnitrenes from the dibenzothiophene chromophore. The synthesis of 1f-g will be addressed further in the chapter, while the main focus is confined to the photochemistry of sulfilimines 1b-e. These sulfilimines are analogs of those studied by Morita, using dibenzothiophene, rather than thianthrene, as the base sulfide. Though we do not directly compare the two systems here, the photochemistry of the thianthrene derivatives$^{23}$ is more complex. The starting materials and potential products deriving from the photolyses are shown in Chart 1. The compounds are numbered such that sulfilimine 1a gives rise to nitrene 2a, which in turn gives rise to potential products 3a, 4a, 5a, and so on.
3.3 Results and Discussion

Time Resolved IR Studies

TRIR methods were used to try to detect the various nitrenes directly. This method faces the limitation that its time resolution is approximately 50 ns; intermediates that are shorter-lived than that cannot be observed. Photolyses of three sulfilimines were carried out
(1b, 1c, and 1d). The mesyl derivative 1d was chosen over the tosyl derivative 1e to reduce the complexity of the spectrum.

**N-acetyl dibenzothiophene sulfilimine, 1b and acetylnitrene 2b.** Recent results with 1a,\(^{21}\) which leads to singlet and triplet benzoylnitrene, provided an anticipated framework from which to interpret results from 1b. TRIR difference spectra obtained on 266 nm laser photolysis of 1b in CD\(_2\)CN and in CD\(_2\)Cl\(_2\) are shown in Figure 1. Corresponding kinetic traces obtained from 266 nm laser photolysis are shown in Figures 2 and 3.

![Figure 1. TRIR difference spectra averaged over 3.6 µs after 266 nm laser photolysis of 1b in argon-saturated (a) CD\(_2\)Cl\(_2\) and (b) CD\(_2\)CN. The bars indicate B3LYP/6-31G(d) calculated value IR frequency (scaled by 0.96) of triplet acetylnitrene, \(^3\)2b.](image)
Figure 2. Kinetic traces obtained at (a) 2255 cm\(^{-1}\) (b) 1776 cm\(^{-1}\) (c) 1680 cm\(^{-1}\) and (d) 1518 cm\(^{-1}\) after 266 nm laser photolysis of 1b in argon-saturated CD\(_2\)Cl\(_2\). The red lines are experimental data and the black curves are the calculated best fit to a single exponential function.

Figure 3. Kinetic traces obtained at (a) 1648 cm\(^{-1}\) (b) 1515 cm\(^{-1}\) and (c) 1780 cm\(^{-1}\) after 266 nm laser photolysis of 1b in argon-saturated CD\(_3\)CN. The red curves are experimental data and the black curves are the calculated best fit to a single exponential function.
Methyl isocyanate was observed at 2255 cm\(^{-1}\). It was produced faster than the 50 ns resolution of the instrument (Figure 2a), consistent with a direct excited state rearrangement of \(1b\) being its source, as was found for the analogous product from \(1a\) (Scheme 1).

![Scheme 1](image)

**Scheme 1.** Proposed photochemical processes for \(1b\) based on IR data.

In dichloromethane, a peak at 1518 cm\(^{-1}\) grows in with a \(~230\) ns time constant and decays over a few microseconds (Figure 2d). We attribute it to \(^3\)2b. B3LYP/6-31G(d) calculations on acetylnitrene predict a strong IR band at 1774 cm\(^{-1}\) for the singlet nitrene and 1500 cm\(^{-1}\) for the triplet nitrene (frequencies scaled by 0.96\(^2\)).

Singlet acetylnitrene was not observed due to an overlapping IR band near 1776 cm\(^{-1}\). The 1776 cm\(^{-1}\) band grows in at the same rate as the triplet nitrene, and this rate depends on the initial concentration of the precursor. The band is attributed to the reaction product between the singlet acetylnitrene and DBT or the starting material. Also, another band at
1680 cm\(^{-1}\) was observed (Figure 2c), which is believed to arise from the singlet nitrene reaction with dichloromethane.

In CD\(_3\)CN, the band at 1776 cm\(^{-1}\) was weak and a new band at 1648 cm\(^{-1}\) was observed. The 1648 cm\(^{-1}\) band was attributed to the formation of acetonitrile-ylide from the singlet acetylnitrene. A strong vibration for this species was calculated at 1694 cm\(^{-1}\), in reasonable, but not outstanding, agreement with the observed value. The decreased intensity of the 1776 cm\(^{-1}\) band is attributed to the competition between acetonitrile ylide formation and reaction of the singlet nitrene with DBT. The decreased intensity of the 1776 cm\(^{-1}\) band enabled us to observe a kinetic trace at 1776 cm\(^{-1}\) which decays at the same rate as the growth of the 1515 cm\(^{-1}\) band and the ylide band. The decay trace at 1776 cm\(^{-1}\) is attributed to singlet acetylnitrene; we believe that the singlet nitrene is the most likely source for the ylide and at least most of the triplet nitrene.

Based on the lack of a literature report of a triplet epr spectrum of acetylnitrene at low temperature and recent calculations at the CBS-QB3 level,\(^{28}\) we presume that the energies of the singlet and triplet states of acetylnitrene are very similar, but that the singlet is slightly lower. Thus, population of the triplet acetylnitrene by the singlet is presumably a relaxation toward that thermal equilibrium, which is then depleted by reactions of either the singlet or triplet nitrene. Product studies (\textit{vide infra}) are consistent with mainly singlet chemistry, but this can be understood in terms of greater rate constants for reaction from the singlet nitrene than from the triplet.

\textit{N-trifluoroacetyl dibenzothiophene sulfilimine 1c and trifluoroacetylnitrene 2c.} Similar TRIR measurements were performed using 1c as the starting material. Typical difference
spectra are shown in Figure 4 in (a) Ar-saturated dichloromethane and (b) Ar-saturated acetonitrile. Kinetic traces for the positive bands in dichloromethane, observed at 1660, 1715, and 2270 cm$^{-1}$, are shown in Figure 5, while kinetic traces for the positive bands observed at 1688, 1218, and 2270 cm$^{-1}$ in acetonitrile are shown as Figure 6. (The kinetic trace of 1460 cm$^{-1}$ is identical to that of 2270 cm$^{-1}$ observed in argon-saturated dichloromethane.)

Figure 4. TRIR difference spectra observed following 266 nm laser photolysis of 1c (1.0 mM) in argon-purged (a) dichloromethane, top and (b) acetonitrile, bottom.
Figure 5. Kinetic traces observed at (a) 1660, (b) 1715, and (c) 2270 cm$^{-1}$ following 266 nm laser photolysis of 1c (1.0 mM) in argon-purged dichloromethane. The dotted-line curves are experimental data and the solid lines are calculated best fits to a single-exponential function.
Figure 6. Kinetic traces observed at (a) 1688 cm$^{-1}$ from –0.4 to 3.6 µs, (b) 1218 cm$^{-1}$ from –0.4 to 3.6 µs, (c) 1688 cm$^{-1}$ from –100 to 900 µs, (d) 1218 cm$^{-1}$ from –100 to 900 µs, and (e) 2270 cm$^{-1}$ following 266 nm laser photolysis of 1c (1.0 mM) in argon-purged acetonitrile. The dotted-line curves are experimental data and the solid lines are calculated best fits to a single-exponential function.

In dichloromethane, the negative band observed at 1624 cm$^{-1}$ is due to depletion of precursor 1c. A positive band observed at 1660 cm$^{-1}$ is formed at a rate faster our
instrumental time resolution (50 ns), and decays at a first-order rate of $6.5 \times 10^4 \text{s}^{-1}$, as shown in Figure 5a. (Note the 1660 cm$^{-1}$ band partly overlaps with the precursor depletion band observed at 1624 cm$^{-1}$.) Additionally, the decay rate of this band is unaffected in the presence of oxygen, suggesting that it is due to a singlet species. The decay rate of 1660 cm$^{-1}$ band is linearly dependent upon the concentration of methanol, indicating a second-order reaction between the carrier and methanol with a second-order rate constant of $k_{\text{methanol}} = 5.0 \times 10^6 \text{M}^{-1} \text{s}^{-1}$. This rate constant is comparable with that of singlet benzoylnitrene reaction with methanol ($6.5 \pm 0.4 \times 10^6 \text{M}^{-1} \text{s}^{-1}$).\textsuperscript{21}

Based on these results, the most reasonable assignment to the 1660 cm$^{-1}$ band is to singlet trifluoroacetylnitrene ($^{1}2\text{c}$). However, we face the difficulty that the B3LYP/6-31G(d) calculations predict intense vibrations at 1304, 1201, and 1189 cm$^{-1}$ (scaled by 0.96) and none near 1660 cm$^{-1}$ for $^{1}2\text{c}$. These calculations predict frequencies at 1611, 1226, 1195, and 1167 cm$^{-1}$ for the triplet nitrene.

Another positive band is observed at 1715 cm$^{-1}$. Its growth rate ($k_{\text{obs}} = 6.5 \times 10^4 \text{s}^{-1}$, Fig 5b) matches the decay of the 1660 cm$^{-1}$ band. This band is not observed in acetonitrile, nor is its appearance rate affected by the concentration of the precursor. It is thus assigned to a reaction product between dichloromethane and the 1660 cm$^{-1}$ intermediate.

In dichloromethane, trifluoromethyl isocyanate $12\text{c}$ is detected at 2270 and 1460 cm$^{-1}$, in good agreement with the 2255 cm$^{-1}$ value observed for $12\text{b}$ and literature reports.\textsuperscript{29} Again, its rate of growth is faster than instrumental resolution (Fig 5c), indicating that its precursor is not the relaxed singlet nitrene, but more likely the excited state precursor $1\text{c}$, or potentially an excited nitrene. In acetonitrile, it is detected similarly at 2270 cm$^{-1}$ (Fig 6e).
In acetonitrile, no band attributable to singlet nitrene was observed. However, we assign two new positive bands observed at 1688 and 1218 cm\(^{-1}\) (Fig 6) to the acetonitrile ylide 18c, formed from singlet nitrene 12c reaction with acetonitrile, in good agreement with B3LYP/6-31G(d) calculated frequencies of 1706 (scaled by 0.96)\(^{30}\) and 1241 cm\(^{-1}\). Both bands are formed more rapidly than instrumental response, and, presumably, decay to oxadiazole 10c at a first-order rate of \(6.5 \times 10^2\) s\(^{-1}\).

In order to confirm this assignment and check for self-consistency, we examined the behavior of the 1660 cm\(^{-1}\) band observed in dichloromethane with respect to smaller added amounts of acetonitrile. Kinetic traces for solutions in dichloromethane containing 1 mM acetonitrile are shown in Figure 7 at frequencies of 1660, 1688, 1715, and 1218 cm\(^{-1}\). The growth rate of the ylide bands at 1688 and 1218 cm\(^{-1}\) is the same as the decay of the 1660 cm\(^{-1}\) band, indicating a kinetic parent-daughter relationship between the two bands. (Note that the 1218 cm\(^{-1}\) band of ylide 18 overlaps with another instantaneous growth band.) Additionally, the rate of decay of the 1660 cm\(^{-1}\) band is linearly dependent on the concentration of acetonitrile, from which a second order rate constant of \(1.5 \times 10^7\) M\(^{-1}\) s\(^{-1}\) can be derived. This is two orders of magnitude larger than the rate constant reported for benzoylnitrene and acetonitrile (\(3.4 \pm 0.6 \times 10^5\) M\(^{-1}\) s\(^{-1}\)).\(^{28}\)
Figure 7. Kinetic traces observed at (a) 1660, (b) 1688, (c) 1715, and 1218 cm$^{-1}$ following 266 nm laser photolysis of 4 (1.0 mM) in argon-purged dichloromethane in the presence of added acetonitrile (1.0 mM). The dotted-line curves are experimental data and the solid lines are calculated best fits to a single- or double-exponential function.

We did not detect any transients easily assignable to the triplet nitrene, but as will be discussed below, product studies are clearly consistent with triplet nitrene reactivity. Albeit the mismatched frequency calculations, it would be straightforward to assign the 1660 cm$^{-1}$ band to $^1$2c, with the $\mu$s-timescale decay of the singlet nitrene in dichloromethane presumably attributable to reaction with solvent, with only a minor if any contribution from intersystem crossing to the triplet nitrene, which is not kinetically observed. This possibility is represented as Scheme 2, an otherwise by-now conventional diagram that does not address the interplay between the two nitrene multiplicity states. It should be noted that it does not
necessarily eliminate the unobserved triplet nitrene $^32c$; there simply is not strong evidence for it from the TRIR experiments.

Scheme 2. A potential reaction scheme for 1c, based on assignment of the 1660 cm$^{-1}$ band to singlet nitrene $^12c$.

Given the lack of a singlet nitrene signal calculated near 1660 cm$^{-1}$ and the existence of one for the triplet nitrene, we must also entertain the possibility that the 1660 cm$^{-1}$ band represents the triplet nitrene. Under this scenario, one must assume that the apparent singlet reactivity (acetonitrile, methanol) is due to rapid equilibration of the two spin states of the nitrene, which draws down the concentration of the triplet. We must also assume an unusually slow reaction between $^32c$ and O$_2$. This might be plausible because of the electron-withdrawing nature of the CF$_3$ group, but is not attractive. Neither of these contrasting assignments is entirely satisfactory, and this scheme is discussed further in the product study section below.

_N-mesyl dibenzo thiophene sulfilimine 1d and mesynitrene 2d_. The TRIR difference spectra obtained on laser photolysis of 1d in Ar-flushed CD$_3$CN are shown in Figure 4 and
corresponding kinetic traces at 1330 cm\(^{-1}\) and 1150 cm\(^{-1}\) are shown in Figure 5. Similar data were obtained in dichloromethane. B3LYP/6-31G(d) calculations on triplet mesylnitrene (\(^3\text{2d}\)) in Cs symmetry predict a strong IR band at 1241 cm\(^{-1}\) and 1058 cm\(^{-1}\). As is evident from the figure, these bands were not observed, though the latter might conceivably be obscured by the observed peak near 1150 cm\(^{-1}\). On computational examination, the singlet nitrene has a stationary point with Cs symmetry, but it is a transition state. Lowering the symmetry to C1 allows a minimum to be found (\textit{vide infra}), and characteristic strong IR bands are predicted at 1134 cm\(^{-1}\) and 1023 cm\(^{-1}\). Neither were these frequencies observed.

\textbf{Figure 4.} TRIR difference spectra averaged over 45 \(\mu\)s after 266 nm laser photolysis of \(1d\) in argon-saturated CD\(_2\)CN.
Figure 5. Kinetic traces obtained at (a) \(1330\, \text{cm}^{-1}\) (b) \(1150\, \text{cm}^{-1}\) and after 266 nm laser photolysis of 1d in argon-saturated CD₃CN.

As is evident from Figures 4 and 5, we observed two strong and permanent bands at \(1330\, \text{cm}^{-1}\) and \(1150\, \text{cm}^{-1}\). We tentatively assign these bands to sulfonylazepine 19 (Scheme 3) arising from the attack of singlet nitrene onto the DBT nucleus, based on the IR measurements of sulfonyl azepine 20 by Paquette. The reported IR frequencies for N-mesyl azepine in CHCl₃ are \(1330\, \text{cm}^{-1}\) and \(1155\, \text{cm}^{-1}\), which is in good agreement with the observed TRIR signals. (In order to be consistent with product study data, we must also assume that the azepine rearranges to the net C-H insertion products 5c on a longer timescale.) Both these bands were produced at a timescale faster than the instrument resolution (50 ns). Furthermore, it is long established that 20 and related derivatives easily rearrange to the corresponding N-phenylmethanesulfonamides, and product studies (vide infra) show formation of such rearranged products, e.g., 5. We infer that the short-lived singlet nitrene is responsible for this chemistry, assuming the assignment is correct. We did not observe the triplet nitrene on this timescale, but these negative results do not necessarily rule out its formation.
Scheme 3. Potential trapping of singlet mesylnitrene, 2

Product Studies

*N*-Acetyl dibenzothiophene sulfilimine, 1b. Representative product study results for photolysis of 1b are shown in Table 1. The observed products indicate a predominance of singlet chemistry. For example, stereochemistry of the alkene is preserved in the formation of aziridines from 4-octenes in acetonitrile (entries 1 and 2).\textsuperscript{32} Potential products 4b, 10b, and 12b were not detected in these experiments. They could have been formed, but because of the concentration of the sample before analysis, may have evaporated and been missed.

The reaction with iPrOH as solvent is dominated by O-H insertion, rather than hydrogen abstraction (entry 3), also consistent with singlet chemistry. Entry 3 also shows evidence for formation of the isocyanate, as seen by formation of 13b. These results are broadly consistent with those we recently reported for benzoylnitrene generated by photolysis of 1a.\textsuperscript{33}
Table 1. Product yields from photolysis of 1b.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>( \lambda_{ex}, ) nm</th>
<th>( \Phi_{DBT} )</th>
<th>Product yields (%)</th>
<th>( \text{Cis} )</th>
<th>( \text{trans} )</th>
<th>4b</th>
<th>6b</th>
<th>10b</th>
<th>12b</th>
<th>13b</th>
<th>14b</th>
<th>U&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10% cis-4-octene in CH&lt;sub&gt;3&lt;/sub&gt;CN&lt;sup&gt;a&lt;/sup&gt;</td>
<td>320</td>
<td>0.49</td>
<td>54</td>
<td>0</td>
<td>nd&lt;sup&gt;b&lt;/sup&gt;</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10% trans-4-octene in CH&lt;sub&gt;3&lt;/sub&gt;CN&lt;sup&gt;a&lt;/sup&gt;</td>
<td>320</td>
<td>0.69</td>
<td>0</td>
<td>61</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>iPrOH-( d_8 )</td>
<td>320</td>
<td>0.62</td>
<td>(&lt;1)</td>
<td>72</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4&lt;sup&gt;c&lt;/sup&gt;</td>
<td>CD&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>320</td>
<td></td>
<td>24</td>
<td>30</td>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10% MCH&lt;sup&gt;f&lt;/sup&gt; in CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>320</td>
<td>0.91</td>
<td>27</td>
<td>31</td>
<td>5</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10% MCH in CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>350</td>
<td>X&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.62</td>
<td>61</td>
<td>6</td>
<td>6</td>
<td>22</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Product yields determined from \(^1\)H NMR integration of the concentrated photosylate.  
<sup>b</sup>Not determined.  Volatile materials that were not observed after evaporation of solvent, but may have been in the mixture originally.  
<sup>c</sup>Overall yield of 14b and isomers of 14b.  The illustrated tertiary product 14b identified by comparison with authentic sample using GC.  Other isomers of 14 were identified based on their GC-MS data.  
<sup>d</sup>Xanthone (ca. 4 mM) sensitized photolysis.  
<sup>e</sup>Uncharacterized product: percentage reported from \(^1\)H-NMR integration of the peak at 2.31 ppm.  
<sup>f</sup>methylcyclohexane.

In CD<sub>3</sub>CN without any additional trapping agent, where evaporation before NMR analysis is not necessary, the cyclized product 10b and methyl isocyanate 12b are detected directly, along with an unidentified adduct.  The assignment of 12b is based on the appearance of a methyl singlet at 2.98 ppm in the \(^1\)H NMR.  The unidentified compound (in entries 4-6) has a methyl peak at 2.31 ppm, consistent with an acetamide derivative, presumably an adduct to DBT.
Photolysis in acetonitrile with methylcyclohexane provides the same unidentified adduct. It also affords some C-H insertion product due to reaction with methylcyclohexane. The major isomer detected was the illustrated isomer of 14b, i.e., the result of the insertion into the single 3° CH position (as determined with authentic sample). None of the product due to insertion into a primary C-H bond was observed (authentic sample), but other minor GC-MS peaks were assigned to some of the 10 possible secondary C-H insertions. Authentic samples were not obtained for these. The high selectivity for tertiary insertion is consistent with very early work by Lwowski using different precursors and dimethylcyclohexane. In that work the retention of the methyl stereochemistry in the inserted product was used as evidence for singlet-based chemistry.34 (Hadad and Platz report a computed barrier of 14-19 kcal/mol (depending on method) for the insertion of 12b into the 2-position of propane.28)

Xanthone-sensitized photolysis (entry 6) also leads to the formation of the tertiary C-H insertion product 14b and a greater proportion of the cyclized product 10b over methyl isocyanate than when direct irradiation is used. The presence of any isocyanate at all may be evidence for some direct photolysis, even under these conditions, according to the TRIR experiments. However, the predominance of the singlet reactions is also consistent with the equilibration between the singlet and triplet nitrene states, as proposed in the IR section.

N-Trifluoroacetyl dibenzothiophene sulfilimine, 1c. The results of product studies with 1c contrast dramatically with those of 1b. They unambiguously demonstrate the intervention of a triplet intermediate, presumably 32c from an analytical perspective, though, some adaptations had to be made to obtain the data. The lack of a methyl handle on the
products and their volatility on concentration of solvent led to the use of \(^{19}\)F NMR as the principle analytical method for the experiments reported in Table 2.

**Table 2.** Product yields on photolysis of 1c.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>(\Phi_{\text{DBT}})</th>
<th>Purge</th>
<th>Product yields (%) relative to DBT(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{cis-3c})</td>
</tr>
<tr>
<td>1</td>
<td>0.89 M cis-4-octene in CD(_3)CN(^c)</td>
<td>0.08</td>
<td>Ar</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>0.89 M trans-4-octene in CD(_3)CN(^c)</td>
<td>0.09</td>
<td>Ar</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>0.89 M cis-4-octene in CD(_3)CN(^c)</td>
<td></td>
<td>O(_2)</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>0.89 M trans-4-octene in CD(_3)CN(^c)</td>
<td></td>
<td>O(_2)</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>0.012 M cis-4-octene in CD(_3)CN(^c)</td>
<td></td>
<td>Ar</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>0.012 M trans-4-octene in CD(_3)CN(^c)</td>
<td></td>
<td>Ar</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>(i)-PrOH (d8)</td>
<td></td>
<td>Ar</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Excitation at 320 nm. Yields determined from \(^{19}\)F NMR integration of photosylate spectra, using Freon 113 as an internal standard. Trace yields are indicated as "tr". Unquantified, but GC-MS identified yields are identified as "+". \(^b\)Tentatively identified as 10e based on \(^{19}\)F NMR. See text. \(^c\)Other uncharacterized product peaks also observed. \(^d\)Difficult to quantify precisely, \(ca. 70\%\). There were many small, uncharacterized peaks.

The assignment of the identity 10c is circumstantial. The observed \(^{19}\)F signal (\(\delta\) -66.8) differs by 21 ppm from that of trifluoromethyl isocyanate, eliminating that as a possibility. The fact that the relative yield of 10c increases on addition of O\(_2\) implies that it is a singlet-derived product. Its absence in \(i\)-PrOH (entry 8) is consistent with 10c containing the elements of acetonitrile. Although we are unaware of any literature preparation or
unambiguous characterization of 10c, three other related compounds were found that had similar $^{19}$F chemical shifts:

Thus, by chemical analogy to the previous derivatives, and spectroscopic analogy, we assign the observed compound and its -66.8 ppm $^{19}$F NMR peak to the structure 10c.

The cis aziridine was identified by both $^1$H and $^{19}$F spectra, compared to authentic samples. The trans aziridine was identified by spectroscopic analogy to other cis and trans aziridine pairs. The stereochemistry of the alkenes is only partially retained in the aziridines (entries 1-4).

The use of acetonitrile as a solvent with alkene concentrations near 1 M provided conditions in which direct reaction of 12c would be competitive with the alkene and solvent, based on the precedent of the Platz data for benzoylnitrene. (We do not know if the ylide 18c would react with alkene to form aziridine, but are confident that stereochemistry would be retained if so.) Thus, these conditions provided an excellent chance to observe triplet nitrene reactivity, in the form of lost stereochemistry in the aziridines. The results in Table 2, with incomplete retention of alkene stereochemistry in the aziridine products, confirm the presence of 32c in the reaction mixture. The simplest interpretation of the different trans/cis ratios from cis- and trans-4-octenes is that both singlet and triplet nitrene reactivity is being observed. The alternate interpretation — that the triplet nitrene reacts with alkene without
complete loss of stereochemistry — seems unlikely, due to the TRIR experiments that prove the existence of \( ^12c \) in the mixture.

Because the addition of a singlet nitrene to an olefin is expected by all literature precedent to have a much higher rate constant than does addition of a triplet nitrene to an olefin, the very observation of the mixed stereochemistry of the aziridines implies that the ground state of CF\(_3\)CON is probably a triplet, if intersystem crossing between the two states is kinetically competitive. We do not have evidence, however, that eliminates the possibility (see Scheme 2) that the branching between the two spin states of the nitrene is essentially irreversible, i.e., that, once formed, both \( ^12c \) and \( ^32c \) react faster in some other way than they interconvert.

A standard probe to probe for simultaneous reactivity from singlet and triplet nitrenes is to determine the ratio of trans/cis aziridines from varying cis-alkene concentrations.\(^{36}\) Variation in the trans/cis ratio is used to imply that capture of the nitrene by the alkene is kinetically competitive with intersystem crossing. An invariant ratio can indicate either very rapid spin-equilibration (leading to an apparent “single intermediate”) or very slow spin-equilibration, where the initial singlet/triplet branching ratio is maintained throughout the trapping reaction. In the former case of rapid spin-equilibration, the expected result would usually be a predominance of stereochemical retention, because the singlet trapping reaction is expected to be much faster than the triplet reaction. For loss of stereochemistry to predominate, as observed in Table 2, a triplet ground state is required in order that its higher population outweigh the kinetic advantage otherwise held by the singlet.

We believe the lower trans/cis ratio for entry 6, compared to entry 2, is experimentally significant, since the ratio can be determined directly by NMR integration. If so, it implies
that less singlet nitrene is being captured by the lower octene concentration. This is entirely consistent with the singlet nitrene population being drained increasingly to 10c, as observed. The drop in the absolute yield of trans-3c in entry 6 (compared to entry 2) or cis-3c in entry 5, compared to entry 1 further implies that at least some of the triplet nitrene derives from the singlet nitrene.

Addition of O₂ (entries 3 and 4) also provides a small change in product distribution that we believe is experimentally significant. It lowers the overall yield of aziridine (accompanied by an increase in 10c), and also marginally raises the retention of stereochemistry from the alkene to the aziridine, albeit more so when the starting material is trans. Incomplete quenching of 31c would provide this result, assuming that the reaction set out in Scheme 2 is elaborated as in Scheme 4. There is not enough information to determine whether O₂ quenches the triplet nitrene or whether 18c can lead to cis-aziridines.

Scheme 4. Photochemistry of 1c
That triplet reactivity being significant is further implied by the observation of trifluoroacetamide, 4c. Seen in small amounts in the acetonitrile/alkene experiments, it becomes the major product in iPrOH. The expected singlet nitrene adduct 13c was not identified, but we cannot rule out its formation. Many small $^{19}$F signals were observed, and we cannot eliminate the possibility of some formation of the O-H insertion or any other specific products. Nonetheless, the fact that, better than half the mass balance is accounted for by trifluoroacetamide again implies an ultimate predominance in triplet nitrene chemistry.

The product study data thus are strong in pointing toward a predominance of triplet nitrene chemistry in some solvents, and singlet nitrene chemistry in others. Though the combined TRIR and product study data are not conclusive, we favor an interpretation based on assigning the 1660 cm$^{-1}$ IR peak to the singlet nitrene. This implies a certain branching ratio of $^{1}1c^*$ that always provides some minimum amount of triplet nitrene by way of $^{3}1c$, and that more triplet nitrene may be formed if the singlet nitrene is not immediately trapped by solvent. The triplet nitrene is probably lower in energy than the singlet. We acknowledge the difficulty of this otherwise ordinary interpretation with not finding an appropriate frequency near 1660 cm$^{-1}$ in the computational data.

**N-Mesyl dibenzothiophene sulfilimine, 1d.** Time-resolved IR experiments indicated that the likely pathway for formation of the triplet mesynitrene $^{3}2d$ was via the singlet nitrene, $^{1}2d$. The mesyl derivative 1d mainly yielded products attributable to the triplet nitrene on photolysis. The principle results are given in Table 3.
Table 3. Product yields from photolysis of 1d.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>λ, nm</th>
<th>ΦDB</th>
<th>T</th>
<th>Product yields (%), relative to DBT&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cis-3d</td>
</tr>
<tr>
<td>10% cis-4-octene</td>
<td>320</td>
<td>0.08</td>
<td>Ar</td>
<td>28</td>
</tr>
<tr>
<td>in CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% trans-octene</td>
<td>320</td>
<td>0.09</td>
<td>Ar</td>
<td>34</td>
</tr>
<tr>
<td>in CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% trans-octene</td>
<td>320</td>
<td>0.04</td>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>27</td>
</tr>
<tr>
<td>in CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-PrOH</td>
<td>320</td>
<td></td>
<td>Ar</td>
<td>81</td>
</tr>
<tr>
<td>CD&lt;sub&gt;3&lt;/sub&gt;OD</td>
<td>320</td>
<td></td>
<td>Ar</td>
<td>80</td>
</tr>
<tr>
<td>10% cyclohexane</td>
<td>320</td>
<td>0.06</td>
<td>Ar</td>
<td>81</td>
</tr>
<tr>
<td>in CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% cyclohexane</td>
<td>320</td>
<td></td>
<td>Ar</td>
<td>80</td>
</tr>
<tr>
<td>in CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% cyclohexane</td>
<td>350,</td>
<td>0.94</td>
<td>Ar</td>
<td>76</td>
</tr>
<tr>
<td>in CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>X&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Product yields determined from <sup>1</sup>H NMR integration of the concentrated photosylate.  
<sup>b</sup>Combined percentages of 4d and 5d reported due to overlapping CH<sub>3</sub> protons in the <sup>1</sup>H NMR spectrum of the concentrated photosylate (entries 1-3 only).  
<sup>c</sup>Upper limit reported due to other overlapping peaks in the <sup>1</sup>H NMR.  
<sup>d</sup>Xanthone (ca. 4 mM) sensitized photolysis.  
<sup>e</sup>Formed in the photolysis and characterized by GC-MS, but not rigorously quantified.

In acetonitrile/octene (entries 1-3), the trans to cis ratio of aziridines indicates equilibration of stereochemistry in large part, and thus at least mainly triplet addition. In these solvents, both methanesulfonamide 4d (the double hydrogen abstraction product) and an adduct between the mesylnitrene and DBT (5d) were observed in modest yield. Because of overlap in the NMR spectrum of the corresponding methyl groups and the multiple peaks in the aromatic region, the two product yields could not be further distinguished. The adduct
was identified as a formal C-H insertion product by the appearance of HPLC peaks that had UV spectra essentially identical to DBT. We did not determine the regiochemistry of the insertion.

Variation of the alkene concentration gave results consistent with the triplet nitrene deriving from the singlet. (The TRIR data do not speak to this, as neither nitrene was observed.) As shown in Table 4, raising the initial \( \text{cis} \)-alkene concentration from 12 mM to 890 mM not only increased the total aziridine yield, but also increased the retention of stereochemistry modestly. This implies that at least some of the triplet nitrene is formed by way of a slightly higher-energy singlet nitrene, and that intersystem crossing from the singlet nitrene down to the ground state is kinetically competitive with addition by the singlet nitrene to the alkene.

Table 4. Product yields from photolysis of 1d in varying \( \text{cis} \)-4-octene concentrations in dichloromethane.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>[cis-4-octene], M</th>
<th>Aziridine yield(^b)</th>
<th>Trans/Cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.012</td>
<td>74 ± 2</td>
<td>1.87 ± 0.05</td>
</tr>
<tr>
<td>2</td>
<td>0.89</td>
<td>97 ± 3</td>
<td>1.71 ± 0.05</td>
</tr>
</tbody>
</table>

\(^a\)Yields determined from \(^1\)H NMR integration of the concentrated photosylate. Excitation at 320 nm with Ar purge to remove \( \text{O}_2 \). Approximately 18\% 4c was obtained in entry 1. \(^b\)Relative to DBT formation.

On direct photolysis of 1d in methanol (Table 3, entry 5), a nearly quantitative yield of methansulfonamide was obtained. These results are in contrast to those reported by Shingaki \textit{et al.} for photolysis of methanesulfonyl azide.\(^{37}\) In 1:1 cyclohexane/CH\(_2\)Cl\(_2\), they report 18.3\% of the C-H insertion product 8d and 38.4\% of H-abstraction product 4d. In ethanol,
however, they report a 48% of the O-H inserted product and 43.3% of H-abstraction product. These differences may be due either to complexities from one or the other precursors, or perhaps more simply, due to different proportions of initially formed singlet and triplet nitrene (due to varying intersystem crossing and dissociation rates of the different precursors).

N-Tosyl dibenzothiophene sulfilimine, 1e. Upon photolysis of N-tosyl dibenzothiophene sulfilimine, 1e, in the presence of cis or trans-4-octene, we obtained mixed-stereochemistry aziridines (entries 1-4, Table 5). A small degree of stereochemical retention is noted. Again, this could be due to either (a) incomplete equilibration of stereochemistry by the triplet biradical intermediate formed by reaction of the triplet nitrene with the alkene, or (b) reaction by a combination of both singlet and triplet nitrene populations.

The addition of O₂ decreases the overall quantum yield of product formation. Maloney, et al. have reported an unusually fast quenching of triplet sulfonylnitrenes by O₂ (ca. 10⁹ M⁻¹sec⁻¹) based on a transient UV assignment from photolysis of tosyl azide.⁷ The lower quantum yield of DBT formation in the presence of O₂ (Table 5) is consistent with excited state quenching by O₂. However, the lower chemical yields of aziridine (relative to DBT) are also consistent with the trapping of a portion of the nitrene. We suggest that both occur.

Maloney also reported a decrease in the intensity of the transient UV signal when using tosyl azide and adding O₂. While less directly related to the current data (since we do not use
the azide precursor), that observation of precursor triplet quenching is at least consistent with the current results.

**Table 5.** Product yields from photolysis of 1e.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>λ, nm</th>
<th>ΦDB</th>
<th>Product yields (%)</th>
<th>trans/ cis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>3e</td>
<td>4e</td>
</tr>
<tr>
<td>1</td>
<td>10% cis-4-octene in CH3CN</td>
<td>320</td>
<td>0.16</td>
<td>Ar</td>
</tr>
<tr>
<td>2</td>
<td>10% cis-4-octene in CH3CN</td>
<td>320</td>
<td>0.09</td>
<td>O2</td>
</tr>
<tr>
<td>3</td>
<td>10% trans-4-octene in CH3CN</td>
<td>320</td>
<td>0.14</td>
<td>Ar</td>
</tr>
<tr>
<td>4c</td>
<td>10% trans-4-octene in CH3CN</td>
<td>320</td>
<td>0.09</td>
<td>O2</td>
</tr>
<tr>
<td>5</td>
<td>10% cyclohexane in CH3CN</td>
<td>320</td>
<td>0.16</td>
<td>Ar</td>
</tr>
<tr>
<td>6</td>
<td>50% cyclohexane in CH2Cl2</td>
<td>320</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>10% cyclohexane in CH3CN</td>
<td>350</td>
<td>0.73</td>
<td>Ar</td>
</tr>
</tbody>
</table>

*Product yields determined from 1H NMR integration of the concentrated photosylate. †Identified by GC-MS. ‡GC-MS indicates two significant peaks with m/z=169. Xanthone (ca. 4 mM) sensitized photolysis. ‡tr = trace, by GC; "+" = significant but not rigorously quantified (GC).

The standard experiment of examining the effect of alkene concentration on the degree of stereochemical retention in the aziridine was carried out. After some initial experiments gave unexpected results, a new set of carefully controlled measurements were done, all using cis-4-octene as the precursor. As expected, the total yield of aziridine increases with cis-
octene concentration. However, a small but reproducible loss of retention was seen as the alkene concentration was raised (Table 6). Control photolyses of tosyl azide in the presence of cis-4-octene gave intractable mixtures.

Table 6. Product yields from photolysis of 1e in varying concentrations of cis-4-octene in dichloromethane.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>[cis-4-Octene], M</th>
<th>Total aziridines(^b)</th>
<th>trans/cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^c)</td>
<td>0.012</td>
<td>(43 ± 8)%</td>
<td>1.55 ± 0.06</td>
</tr>
<tr>
<td>2</td>
<td>0.071</td>
<td>(70 ± 4)%</td>
<td>1.72 ± 0.04</td>
</tr>
<tr>
<td>3</td>
<td>0.16</td>
<td>(74 ± 3)%</td>
<td>1.81 ± 0.05</td>
</tr>
<tr>
<td>4</td>
<td>0.89</td>
<td>(83 ± 4)%</td>
<td>1.93 ± 0.05</td>
</tr>
<tr>
<td>5</td>
<td>4.30</td>
<td>91</td>
<td>1.9</td>
</tr>
</tbody>
</table>

\(^a\)Excitation at 320 nm, with Ar purging. \(^b\)Relative to DBT formation, by NMR. \(^c\)Significant amounts of 4e were also formed when 0.012 M of cis-4-octene was used.

A singlet ground state for tosylnitrene can be dismissed from the stereochemical results themselves. However, a firm explanation for the data in Tables 5 and 6 is difficult.

If the main precursor for triplet tosylnitrene 3\(^2\)e is 1\(^2\)e and intersystem crossing to 3\(^2\)e is slow or essentially irreversible, the increased cis-alkene concentration should lead to increased cis-aziridine due to the high reactivity of singlet nitrenes with alkenes. This is contradicted by experiment.

- If the main precursor for 3\(^2\)e is 1\(^2\)e and intersystem crossing is extremely rapid and reversible, there should not be much of an effect on the aziridine ratio based on alkene concentration. This is also contrary to the reported result. (Furthermore,
there is no reason to believe isc should be fast and reversible, given the results for all the other nitrenes.)

- If $^3\text{1b}$ (i.e., the excited state of the sulfilimine) reacts with alkene in competition with dissociation to form $^3\text{2e}$, then one has to postulate that this reaction favors the loss of stereochemistry more than does the reaction between $^3\text{2e}$ and the alkene. This seems unlikely, but is possible, and also requires that no more than a minimal amount of aziridine is formed by singlet channels.

Another potential explanation shown in Scheme 5. If the triplet nitrene is born almost exclusively through the triplet excited state of the sulfilimine and $k_s[\text{cis-octene}] > k_{TS}$, then the uphill intersystem crossing step leads to some aziridine with retention. In the limit where $k_{TS}$ becomes essentially irreversible, the degree of retention of stereochemistry is related to 

$$
\frac{k_{TS}}{k_f[\text{octene}] + k_{O_2} + k_{TS}}
$$

If this relation holds, then increasing the octene concentration lowers the retention of stereochemistry because intersystem crossing to the singlet nitrene is competitively suppressed. For the same reason, addition of $O_2$ could also lower the degree of retention if trapping were fast enough; this is observed when comparing entries 4 and 2 of Table 5 to entries 3 and 1, respectively.
In order to probe for singlet reactivity of tosyl nitrene besides the partial retention of stereochemistry of the aziridines, we investigated both alkane solvents and alcohols. Based on lack of radical coupling products and on retention of stereochemistry on insertion, previous workers have attributed alkane insertions observed on thermolysis or photolysis of tosyl azide to reactions of the singlet nitrene.\textsuperscript{9,35} Entries 5 and 6 in Table 5 indicate that only traces of \textit{N}-cyclohexyl tosamide \textit{8e} were observed on photolysis of \textit{1e} in cyclohexane/acetonitrile or cyclohexane/dichloromethane. Instead, the double-hydrogen abstraction product tosamide \textit{4e} was found in high yield. (Reduction of the nitrene is normally considered a triplet nitrene reaction.) This result is analogous to the case of the alkene trapping: a small amount of singlet product in the presence of considerably greater triplet product. Sensitization of \textit{1e} with xanthone (entry 7) did not produce C-H insertion, instead leading to tosamide.

Photolysis of tosyl azide in methanol has been reported to produce the formal OH insertion adduct \textit{7e}. Both the singlet nitrene and the singlet excited state of the azide have been proposed as the key reactive intermediate.\textsuperscript{18,19} We reproduced this result. However, as
shown in Table 7, photolysis of 1e in methanol results instead in nearly quantitative yield of the double-hydrogen abstraction product tosamide 4e.

Table 7. Product yields from photolysis of 1e in alcohols.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Product yields (%)</th>
<th>4e</th>
<th>6e</th>
<th>7e</th>
<th>9e</th>
<th>11e</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>77% t-BuOH in CH$_3$CN$^a$</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>57% t-BuOH in benzene</td>
<td>42</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>i-PrOH</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>MeOH$^b$</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Product yields determined from $^1$H NMR integration of the concentrated photosylate. All samples are Ar purged and $\lambda_{ex} = 320$ nm. $^b$GC-MS trace of the photosylate indicates a trace amount of an isomer of 7e.

A similar result was found in iPrOH, where an authentic sample of adduct 6e was independently prepared just to be sure that no trace product was being overlooked. Tosyl azide has also been reported to produce tosamide quantitatively on photolysis in iPrOH, but the suggestion has been made that this is due to radical chain chemistry.$^4$

In order to remove that ambiguity, we photolyzed 1e in solvent mixtures containing t-BuOH. None of the OH insertion product (9e) was formed, and again a high yield of tosamide was observed with acetonitrile as the cosolvent (entry 1). With benzene as a cosolvent (entry 2), tosamide was formed with smaller yield, and the formal benzene CH insertion adduct 11e was formed competitively. We assume that this adduct is formed by singlet nitrene addition to benzene via the azepine in much the same way that a certain amount of singlet nitrene reacts with the octenes, as described by Scheme 4.
The previously reported results from tosyl azide photolysis in methanol (leading to some singlet product) have been complemented by much higher yields of insertion product (8e) from tosyl azide in cyclohexane, compared to H-abstraction product 4e than we have observed on photolysis of 1e.\(^9\) Instead, we still observed mainly the reduction product (Table 5). We suggest that the sum of our evidence is in favor a much larger proportion of 1e leading to triplet tosylnitrene without intervention of the singlet tosylnitrene than is the case for photolysis of tosylazide.

**Computational Studies**

Theoretical studies on formylnitrene (2h) and acetylnitrene (2b) have been published.\(^{28,39-41}\) Two major features may be extracted from these data: (1) The singlet state of these nitrenes is highly stabilized by an interaction between the in-plane lone pair on O and the empty in-plane orbital on N, resulting in the shortening in the N-O distance and narrowing of the O-C-N angle, relative to the triplet; and (2) The calculated singlet-triplet energy gap is rather method-dependent. For example, among several methods, only CBS-QB3 correctly predicts a singlet ground state for acetylnitrene.\(^{28}\)

The relative stability of the triplet state of these acylnitrenes was overestimated by several kcal/mol by B3LYP/6-31(d).\(^{40}\) The consistency of this error, along with experimental results, was used to conclude that the ground state of benzoylnitrene is a singlet, with this relatively inexpensive method.

We wished to use computational methods to corroborate with the conclusions that might be drawn from the product studies reported above for tosylnitrene, mesylnitrene, and trifluoroacetylnitrene. The implementation of B3LYP (and other computational methods) is
slightly different in GAMESS than in GAUSSIAN; thus we undertook the use of GAMESS with several different methods and basis sets in order to calibrate the results obtained against those of Hadad and Platz (HP),\textsuperscript{28} and then expanded to several other methods for the four compounds under consideration here. In addition to the density functional method, we calculate energy differences using ROHF reference functions at the MP2 and completely renormalized coupled cluster (CR-CC(2,3))\textsuperscript{42,43} methods. Additionally, we examined selected molecules using multireference MP2 methods with MCSCF reference functions.\textsuperscript{44,45} The results of these calculations are given in Table 8, where the values in parentheses are taken from HP.
Table 8. Computed $\Delta E_{S-T}$ of nitrenes 2b, 2c, 2d, and 2e at different levels of theory. A positive value implies a triplet ground state.

<table>
<thead>
<tr>
<th>Method</th>
<th>CH$_3$CON</th>
<th>CF$_3$CON</th>
<th>CH$_3$SO$_2$N</th>
<th>PhSO$_2$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>1.9</td>
<td>6.3</td>
<td>14.1</td>
<td>14.5</td>
</tr>
<tr>
<td>B3LYP/6-311G+(d,p)//B3LYP/6-31G(d,p)</td>
<td>2.1 (4.9)$^b$</td>
<td>6.9</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>B3LYP/6-311G(3df,2p)//B3LYP/6-31G(d,p)</td>
<td>0.3</td>
<td>4.7</td>
<td>12.6</td>
<td>13.1</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pV(D+d)Z//B3LYP/6-31G(d,p)</td>
<td>1.7</td>
<td>6.3</td>
<td>13.2</td>
<td>13.8</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d,p)</td>
<td>0.0</td>
<td>4.7</td>
<td>12.6</td>
<td></td>
</tr>
<tr>
<td>B3LYP/aug-cc-pV(Q+d)Z//B3LYP/6-31G(d,p)</td>
<td>0.1</td>
<td>4.8</td>
<td>12.6</td>
<td></td>
</tr>
<tr>
<td>MP2/6-31G(d,p)</td>
<td>$^c$</td>
<td>-1.3</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>MP2/aug-cc-pVTZ//B3LYP/6-31G(d,p)</td>
<td>$^c$ -8.2</td>
<td>-3.9</td>
<td>5.1</td>
<td>4.1</td>
</tr>
<tr>
<td>CASSCF/6-31G(d,p)$^d$</td>
<td>-9.3</td>
<td>-4.7</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>MCQDPT/6-31G(d,p)//CASSCF/6-31G(d,p)$^d$</td>
<td>2.0</td>
<td>6.1</td>
<td>6.7</td>
<td></td>
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<tr>
<td>CR-CC(2,3)/6-311G(3df,2p)//B3LYP/6-31G(d,p)$^e$</td>
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<td>-0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CR-CC(2,3)/aug-cc-pV(D+d)Z//B3LYP/6-31G(d,p)</td>
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<td>3.7</td>
<td>12.2</td>
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<td>CR-CC(2,3)L/G3Large*//B3LYP/6-31G(d,p)</td>
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<td></td>
<td>15.5</td>
<td></td>
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<tr>
<td>CCSD(T)/6-311+G(d,p)//B3LYP/6-31G(d)</td>
<td></td>
<td></td>
<td>12.8</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d,p)</td>
<td>(1.9)$^b$</td>
<td>(1.6)$^b$</td>
<td>(1.6)$^b$</td>
<td>(1.6)$^b$</td>
</tr>
</tbody>
</table>

$^a$Positive $\Delta E_{S-T}$ values indicate triplet ground states. Spherical harmonics were used on the polarization functions. All data are $\Delta$H (298 K), with temperature corrections unscaled and taken from the Hessian calculated at the optimization method. $^b$Values in parentheses are from reference 28. $^c$Triplet acetylnitrene always gave an imaginary frequency corresponding to the methyl rotations and hence could not locate a minimum on the triplet nitrene surface. $^d$The (6,5) active space for CH$_3$CON includes the carbonyl $\pi$-system, a lone pair on the oxygen and filled and empty $p$-orbitals on nitrogen. The (22,15) active space for mesylnitrene includes all the oxygen and nitrogen lone pairs, and the S-O and S-N sigma bonds. The active spaces are illustrated in Appendix B. $^e$CR-CC(2,3) is also known as CR-CCSD(T)_L.
As can be seen immediately from the table, there is a wide variance in the calculated $\Delta E_{S-T}$ values for any given compound.\textsuperscript{46} However, in contrast to results for formylnitrene,\textsuperscript{50} there is only a fairly modest dependence of $\Delta E_{S-T}$ – approximately 2 kcal/mol – on the basis set (at least at the B3LYP level) for any of the present nitrenes. This is, presumably, due to fairly efficient cancellation of errors when comparing the singlet and triplet species. Especially notable is that data obtained with the 6-311G(3df,2p) basis set are within about 1 kcal/mol of those from the aug-cc-pV(T+d)Z basis set, and often much closer than that. The cc basis set is computationally much more expensive, but of similar (though not identical) quality in terms of polarization and having a triple-zeta valence shell. Thus, we infer that the data for the coupled cluster calculations at the latter, larger basis set would be similar to the ones reported in Table 8.

However, the correlation picked up by each method for the different multiplicity states varies (and is not cancelled out); thus the variation is larger between methods. As noted previously, we expect that the density functional values are too positive by several kcal/mol.

Some specific discussion of the CASSCF calculations is required. Careful choice of active space is required to ensure that the calculations are on equal footing for singlet and triplet states of the nitrenes. For the two carbonylnitrenes, an active space of 6 electrons in 5 orbitals was sufficient. These included the carbonyl $\pi$ system, a lone pair on the oxygen, and the filled and empty $p$-orbitals on N at the beginning of the calculation, and these orbitals are approximately preserved in the triplet states (see Appendix B). In the singlet state, the geometric distortion leads to formation of a partial single bond between the N and O, but the general locations of the orbitals is the same. The geometries obtained by optimizing at the CASSCF are quite similar to those obtained at the B3LYP level, and vibrational analysis
showed them to be minima. For mesylnitrene, after extensive experimentation, the only satisfactory active space was 22 electrons in 15 orbitals (Appendix B). This corresponds to a full valence active space on the SO$_2$N fragment of the molecule. Again, the resulting geometries were very similar to that from B3LYP, and vibrational analysis proved the structures to be minima.

As noted by HP, the B3LYP density functional overestimates the relative stability of the triplet state by several kcal/mol, leading to an incorrect prediction of ground state multiplicity for acetylnitrene. The true $\Delta E_{S-T}$, while its exact magnitude remains unknown, is surely slightly negative. We obtain a singlet ground state using multireference MP2, and approximate degeneracy of the states by the coupled cluster method. (Based on the B3LYP data, a better basis set would likely have made $\Delta E_{S-T}$ more negative.)

Despite this uncertainty in the absolute value of $\Delta E_{S-T}$, even for acetylnitrene, the data in Table 8 show that the increments from one compound to the next are approximately the same, regardless of the computational method. For example, the $\Delta E_{S-T}$ values for CF$_3$CON are consistently 4-5 kcal/mol more positive than those for CH$_3$CON. This places, from a computational point of view alone, the ground state multiplicity of CF$_3$CON in doubt, and the safest conclusion seems to be that the singlet and triplet are nearly degenerate, i.e., the singlet nitrene is somewhat less stabilized by the adjacent carbonyl when the hydrogens have been substituted by fluorines.

It also seems safe to suggest that the computations show that both mesyl and tosyl nitrene (or its stand-in for Table 8, benzenesulfonylnitrene) have triplet ground states. Furthermore, the "insulation" provided by the sulfonyl group means that the $\Delta E_{S-T}$ is not so different between the two. It is not practical yet to carry out extraordinarily high level
calculations for benzenesulfonylnitrene. However, the consistency of the data at the B3LYP and MP2 level with those of mesynitrene give us confidence that higher level calculations would give similar results.

Figure 6 illustrates the geometric result common to both mesynitrene and benzenesulfonylnitrene: the triplet states have symmetric geometries common to other sulfonyl derivatives, but the singlet states have distorted geometries that indicate significant bonding interaction between the O and N. Key geometric parameters for all four nitrenes are given in Table 9. Also shown are the Mulliken bond orders, taken from the B3LYP/6-31G(d,p)\(^{47}\).

**Figure 6.** Calculated Geometries for Mesynitrene, calculated at B3LYP/6-31G(d,p) level. The view down the S-C axis obscures the carbon atom; the methyl hydrogens are visible.
Table 9. Key Calculated Geometric Parameters. Mulliken Bond Orders are given in parentheses.

<table>
<thead>
<tr>
<th>Nitrene</th>
<th>$r_{\text{c}=\text{o}}$ or $r_{\text{S}=\text{O}}$, Å</th>
<th>$r_{\text{C}=\text{N}}$ or $r_{\text{S}=\text{N}}$, Å</th>
<th>$r_{\text{O}=\text{N}}$, Å</th>
<th>$r_{\text{S}=\text{O}}$, Å</th>
<th>$\angle \text{OCN}$ or $\angle \text{OSN}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\text{CH}_3\text{CON}$</td>
<td>1.31 (1.12)</td>
<td>1.26 (1.66)</td>
<td>1.77 (0.87)</td>
<td></td>
<td>86.9</td>
</tr>
<tr>
<td>$^3\text{CH}_3\text{CON}$</td>
<td>1.23 (1.88)</td>
<td>1.40 (1.12)</td>
<td>2.25 (0.18)</td>
<td></td>
<td>117.7</td>
</tr>
<tr>
<td>$^1\text{CF}_3\text{CON}$</td>
<td>1.30 (1.15)</td>
<td>1.26 (1.64)</td>
<td>1.81 (0.87)</td>
<td></td>
<td>89.8</td>
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<tr>
<td>$^3\text{CF}_3\text{CON}$</td>
<td>1.22 (1.87)</td>
<td>1.39 (1.12)</td>
<td>2.27 (0.17)</td>
<td></td>
<td>121.4</td>
</tr>
<tr>
<td>$^1\text{CH}_3\text{SO}_2\text{N}$</td>
<td>1.56 (1.06)</td>
<td>1.58 (1.29)</td>
<td>1.77 (0.75)</td>
<td>1.45 (1.78)</td>
<td>68.9</td>
</tr>
<tr>
<td>$^3\text{CH}_3\text{SO}_2\text{N}$</td>
<td>1.47 (1.70)</td>
<td>1.72 (0.89)</td>
<td>2.56 (0.12)</td>
<td>1.47 (1.70)</td>
<td>106.7</td>
</tr>
<tr>
<td>$^1\text{PhSO}_2\text{N}$</td>
<td>1.56 (1.05)</td>
<td>1.58 (1.27)</td>
<td>1.76 (0.76)</td>
<td>1.46 (1.76)</td>
<td>68.3</td>
</tr>
<tr>
<td>$^3\text{PhSO}_2\text{N}$</td>
<td>1.47 (1.68)</td>
<td>1.71 (0.92)</td>
<td>2.55 (0.12)</td>
<td>1.47 (1.68)</td>
<td>106.4</td>
</tr>
</tbody>
</table>

All data obtained from B3LYP/6-31G(d,p) optimizations, including bond order indicies (BOI).

The geometries and bond orders reveal an interesting story. The S-O bond lengths and bond orders for $^3\text{CH}_3\text{SO}_2\text{N}$ and $^3\text{PhSO}_2\text{N}$ are in reasonable agreement with "ordinary" sulfonyl compounds; the bond orders of approximately 1.7 include the traditional sigma bond and the interaction represented either as the second bond in many drawings or the "ylidic" portion of the bond if written in that style. (See, for example ref 48.) However, the bond orders are dramatically different for the singlet sulfonylnitrenes. One S-O bond remains approximately the same as before, but the other is lengthened and weakened. The S-N bond is shortened and strengthened to be above the level of a "single" bond, and of course a much more significant O-N bond order index is achieved: 0.75, vs. <0.2 for the other O-N or for
the triplet states. This set of results can be rationalized by the following picture for the singlet nitrene state, based on the ylide representation of sulfur oxides:

The O-N bond order indices for the carbonylnitrenes are fractionally higher than those for the sulfonylnitrenes, perhaps reflective of the greater singlet-state stabilization in the carbonylnitrenes. There is more, however, to analyze for the carbonylnitrenes. On going from the triplet to singlet state, the carbonyl bonds lengthen and the bond order indices drop significantly, from about 1.9 to nearly 1.1. Additionally, the C-N bond order rises substantially, and of course the O-N bonding order index goes up from a small value (<0.2) to almost 0.9. The lengths change in concert with these bond order indices. Taken together, these structural parameters confirm that the structural character of the singlet carbonylnitrene resembles the substituted oxazirene more than the dipolar structure that more obviously shows the origin of the stabilizing interaction.

The OCN bond angle for $^1$CF$_3$CON is marginally less acute than that for $^1$CH$_3$CON, and the O-N distance is correspondingly a bit longer. These geometric parameters correlate
well with the observed trends in $\Delta E_{ST}$ data, though we will not make the error of ascribing cause and effect with this level of analysis.

The comparison of the carbonylnitrenes to the sulfonylnitrenes, however, does merit discussion. Fundamentally, the question with the sulfonyl group was whether the adjacent oxygen atom could provide the level of stabilization to the closed-shell state of the nitrene as is seen from adjacent carbonyls. In retrospect, perhaps the negative result might have been predicted, based on standard S-N and S-O lengths, vs. C-N and C-O bond lengths. Simply put, the expansion of the S-N and S-O lengths (relative to the C-N and C-O lengths in the carbonylnitrenes) means that the third edge of that triangle must also be longer, assuming a common angle. However, the O-N distances in the singlet sulfonylnitrenes and carbonylnitrenes are comparable. Given that the "third edge" of that triangle, i.e., the O-N interaction/bond, is just as short as in the carbonyl case, then the O-S-N angle must be more acute, presumably introducing more strain. Indeed, the angle is more acute, by almost 20 degrees.

But if we are to even qualitatively rely on strain as an argument, we must address how much strain is introduced by the bending. We cannot know that with certainty from the current data. However, the contraction from triplet to singlet states can be used as a guide: the carbonylnitrene OCN bond angle contracts by a 31-32 degrees on going from triplet to singlet, whereas the sulfonyl nitrenes have a corresponding 38-39 degree contraction. A more complete energy surface calculation would be required to establish the causality of this association. However, the fact that the difference between the two types of functionality is in the bond angle, rather than the N-O distance is clearly established.
3.4 Summary

The data presented here indicate that the dibenzothiophene sulfilimine platform is a useful one for observation of nitrenes with electron-withdrawing substituents. Direct observation of two nitrenes now (benzoylnitrene and acetylnitrene) with TRIR complement the product studies. While not quantitative, the mass balances reported here are at least in line with and much better than many reports of product studies using azide precursors. In the following paragraphs, we attempt to correlate information derived from each of our techniques – spectroscopic, product study, and computational – to provide insight to the dynamics of nitrene formation from sulfilimines 1b-1e, and comment, as appropriate, on the chemistry of the nitrenes themselves.

*N*-Acetyl dibenzothiophene sulfilimine. Previous work on this nitrene is consistent with a singlet ground state. Certainly, nothing in our product studies contradicts this; we see no evidence of triplet reactivity. The computations we have carried out are in line with those of HP, in that they are very method-dependent and predict $\Delta E_{ST}$ to be only a few kcal/mol, regardless of sign. Of the four compounds we examined, only this one gave only singlet nitrene products, and its calculated $\Delta E_{ST}$ is also the most negative among them. Importantly, the triplet-sensitized products are also singlet-derived, which implies that intersystem crossing from the triplet nitrene to the singlet nitrene is downhill (and faster than reaction by the triplet). The evidence from the TRIR is that the triplet state of the nitrene is populated slowly (on the sub-µs timescale), which we take to be thermal population from the singlet nitrene. We thus conclude also that the ground state of acetylnitrene is a singlet, and that it is the only of the four nitrenes reported here for which that is true.
**N-Trifluoroacetyl dibenzothiophene sulfilimine.** Calculations on trifluoroacetylnitrene imply a more positive $\Delta E_{st}$ than for acetylnitrene by about 5 kcal/mol. The product study results indicate a predominance of triplet-derived products (reduction product, loss of stereochemistry in formation of aziridines, etc.). Despite the ambiguity in the direct detection of the intermediates, we can tentatively infer a triplet ground state for the nitrene from these results. We have no reason to believe that the usual pattern of faster rate constants for singlet reactions over triplet reactions would be broken, and thus assume that the triplet products indicate that the nitrene spends significant time in the triplet state. While that could be assigned also to initial formation of the nitrene in the triplet state, followed by slow intersystem crossing to the ground singlet, that hypothesis seems to be contradicted by the data in Table 3. Those data indicate that the singlet nitrene is (at least a partial) precursor to the triplet nitrene, and not the reverse. Thus, we conclude that the ground state of trifluoroacetylnitrene is a triplet. A corollary, if we may assume that the errors in calculated $\Delta E_{st}$ are similar for acetylnitrene and trifluoroacetylnitrene, is that the singlet-triplet energy gap for both nitrenes is less than about 5 kcal/mol, regardless of sign.

**N-mesyl dibenzothiophene sulfilimine and mesynitrene.** It is unfortunate that we were unable to detect either nitrene on photolysis of this sulfilimine in the IR, because this degrades the certainty with which the chemistry can be assigned to that intermediate. However, based on the precedent of the acetyl and benzoyl analogs, along with the product study results, we are willing to conclude that the nitrene is formed. Computational results indicate a triplet ground state by perhaps as much as 10 kcal/mol. However, the product studies clearly indicate a certain amount of "singlet product" in the form of some retention of
stereochemistry in the aziridines and formation of the heterocycle $10d$, which clearly derives from cyclization of the acetonitrile ylide. To rationalize these product distributions, it is necessary to rely on the precedent of slow singlet-to-triplet intersystem crossing of related nitrenes,$^{3,21}$ and the assumption that reaction of the singlet nitrene is kinetically competitive with downhill intersystem crossing.

*N-tosyl dibenzothiophene sulfilimine and tosyl nitrene.* The computational results for tosyl nitrene and mesyl nitrene are so similar that they indicate that there is little "communication" between the phenyl (or methyl) and the nitrene center. We again conclude that a triplet ground state is correct for this nitrene, consistent with the previous reports of epr data from photolysis of tosyl azide at low temperature. Again, however, the product data show some singlet chemistry. In this instance, we see an unusual dependence of the aziridine stereochemistry on the concentration of the alkene, in which raising the concentration of the alkene leads to a decrease in retention. In Scheme 4, we presented a speculative explanation for this phenomenon, in which we suggest that most of the nitrene is formed initially in the triplet state. With sufficiently slow triplet reactivity with the alkene and modest $\Delta E_{ST} \leq 10$ kcal/mol, one could imagine thermal population of the singlet nitrene on the $\mu$s timescale, which would accommodate the data easily. However, it does require that little if any singlet nitrene is formed on direct photolysis, a result that is not common to the other analogs in this series. That said, the alcohol trapping results (Table 7), which show no typical singlet O-H insertion product, regardless of conditions, is also unique to this compound.
3.5 Experimental Section

**Time Resolved IR methods.** The TRIR experiments have been conducted following the method of Hamaguchi and coworkers, as previously described.\textsuperscript{49-51} In short, the broadband output of a MoSi\textsubscript{2} IR source (JASCO) is crossed with excitation pulses from either a Quantronix Q-switched Nd:YAG laser (266 nm, 90 ns, 0.4 mJ) operating at 200 Hz or a Continuum Minilite II Nd:YAG laser (266 nm, 5 ns, 2 mJ) operating at 15 Hz. Changes in IR intensity are monitored using an ac-coupled mercury/cadmium/tellurium (MCT) photovoltaic IR detector (Kolmar Technologies, KMPV11-J1/AC), amplified, digitized with a Tektronix TDS520A oscilloscope, and collected on a Macintosh with IGOR for data processing. The experiment is conducted in dispersive mode with a JASCO TRIR 1000 spectrometer.

**Computational Methods.** Vibrational frequencies for the TRIR experiments were calculated at B3LYP/6-31G(d), using the GAUSSIAN 98\textsuperscript{52} suite of programs. All other computations were carried out using the GAMESS\textsuperscript{53} suite. The output of the GAMESS calculations was visualized using MacMolPlt.\textsuperscript{54} Initial geometries for the GAMESS runs were obtained from semiempirical or HF runs done with Spartan.\textsuperscript{55} Triplet calculations were based on ROHF wave functions. The coefficients and exponents for the G3Large basis set were obtained from http://chemistry.anl.gov/compmat/g3theory.htm. All stationary points, except as noted, are confirmed as energy minima on the potential energy surface by vibrational frequency analysis. The notation G3Large* refers to the use of the G3Large basis set on key atoms S, O, and N and the use of 6-31G(d) on carbon and hydrogen.
Steady State Photolysis Methods. Solvents were spectral grade and were used without further purification. The quantum yield measurements were carried using a 75 W Xe arc lamp fitted to a monochromator set to the specified wavelength with ± 12 nm linear dispersion. Azoxybenzene was used as the actinometer.\textsuperscript{56} Samples were placed in a 1 cm square quartz cell mounted on a holder such that all the light exiting the monochromator hits the sample directly. Except as noted, initial concentrations were 1-4 mM and the solutions were bubbled with Ar for at least 10 min to remove O\textsubscript{2} prior to photolysis. The progress of reactions was monitored by HPLC, using a diode array UV/vis detector with a C18 reverse phase column for separation. All reported yield data represent at least duplicate experiments, and most were carried out in triplicate or greater.

Quantum yields for appearance of dibenzothiophene were determined using HPLC detection with reactions carried out only to low conversion. Product yields were determined from reactions run to nearly complete conversion of starting materials. Identification and quantification were done by a combination of \textsuperscript{1}H-NMR, \textsuperscript{19}F-NMR and GC-MS (EI, DB-5 column) on concentrated reaction mixtures. All compounds, save for \textit{trans}-3, were compared to authentic samples. Previous literature\textsuperscript{35} with both \textit{cis} and \textit{trans} isomers of analogs provided clear precedent for assignment of the aziridine stereochemistry by \textsuperscript{1}H NMR.

Compound Preparation

Products 7\textit{e},\textsuperscript{57} 8\textit{e},\textsuperscript{58} 8\textit{d},\textsuperscript{58} 10\textit{b},\textsuperscript{59} and 11,\textsuperscript{58} were prepared using literature methods. The compounds \textit{cis}-3 were prepared from 4-octene by analogy for a preparation based on 3-hexene.\textsuperscript{35} Compound 6\textit{b} was prepared using a method given for the benzoyl analog.\textsuperscript{60} Its
water solubility and relatively high volatility made purification beyond about 75% difficult, but the NMR data were clear, and the photosylates were clearly identified as identical by spiking the samples with the synthetic mixture. Similarly, urethane 13, prepared by treatment of isopropoxycarbonyl imidazole with excess methylamine in water, could not be completely purified, but was spectroscopically and chromatographically identified. NMR data for previously unreported aziridines and 6b are given in Appendix B.

**N-Acetyl dibenzothiophene sulfilimine, 1b.** To a solution of trifluoroacetic anhydride, (0.14 mL, 1 mmol) in dichloromethane (40 mL) at −78 °C, was slowly added dibenzothiophene-S-oxide (0.1 g, 0.5 mmol) in dichloromethane (3 mL). After cooling and stirring at -78 °C for 1h, powdered acetamide (80 mg, 1.3 mmol) was added as the solid. After 2 h, the reaction was warmed to -20 °C and then quenched with ice water. The reaction mixture was extracted with saturated sodium bicarbonate, and the organic layer was dried and concentrated to give the crude product. The title compound was obtained in 30% yield after silica chromatography with a gradient of ethyl acetate in dichloromethane. ¹H-NMR (CDCl₃) δ 8.01 (d, J = 7.2 Hz, 2H), 7.83 (d, J = 6.9 Hz, 2H), 7.62 (t, J = 7.8 Hz, 2H), 7.52 (t, J = 7.5 Hz, 2H), 2.18 (s, 3H). ¹³C NMR (CDCl₃) δ 24.2, 123.7, 129.0, 130.6, 133.3, 138.4, 182.2.

**N-Trifluoroacetyl dibenzothiophene sulfilimine, 1c.** The compound was prepared as was 1b, save for use of trifluoroacetamide in place of acetamide. 65% yield. ¹H-NMR (CDCl₃) δ 8.18 (d, J = 7.8 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H), 7.74 (t, J = 7.8 Hz, 2H), 7.60 (t,
$J = 7.5 \text{ Hz, 2H}$. $^{13}$C NMR (CDCl$_3$) $\delta$, 117.1 (q, $J = 286.2$ Hz), 122.9, 129.28, 130.7, 133.6, 135.9, 138.7, 169.0 (q, $J = 35.3$ Hz).

**N-Mesyl dibenzothiophene sulfilimine, 1d.** The above procedure was used, save with chloramine M in place of chloramine T. The crude product was purified using column chromatography on silica with 15% ethyl acetate in dichloromethane. The yield of the pure compound was 54%. $^1$H-NMR (CDCl$_3$) $\delta$ 3.08 (s, 3H), 7.6 (t, $J = 7.5$ Hz, 2H), 7.711 (t, $J = 7.5$ Hz, 2H), 7.93 (d, $J = 7.2$ Hz, 2H), 8.03 (d, $J = 7.5$ Hz, 2H). $^{13}$C NMR (CDCl$_3$) $\delta$ 43.5, 122.9, 127.7, 130.5, 133.4, 137.6, 138.3.

**N-Tosyl dibenzothiophene sulfilimine, 1e.** Chloramine T (1.53 g, 6.57 mmol) and DBT (1.00 g, 5.43 mmol) were added to 15 mL methanol. To this solution was added, dropwise, 1 mL glacial acetic acid. The resulting solution was heated to 50 °C with stirring. After about 14 h, the reaction mixture was poured into 10% aqueous NaOH on ice. This solution was filtered and recrystallized from methanol and water to give the title compound in 33% yield. $^1$H-NMR (CDCl$_3$) $\delta$ 2.44 (s, 3H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.87 (d, $J = 9$ Hz, 2H), 7.65 (t, $J = 7.8$ Hz, 2H), 7.63 (t, $J = 6.3$ Hz, 2H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.25-2.28 (m, 2H). $^{13}$C NMR (CDCl$_3$) $\delta$ 21.8, 122.7, 126.9, 127.8, 128.5, 129.6, 130.3, 133.2, 137.7, 137.5.

**N-unsubstituted dibenzothiophene sulfilimine, 1f.** To 0.18g of 1c (0.6 mmol) in ethanol was added NaBH$_4$ (0.023g, 0.6 mmol) and the reaction was allowed to stir overnight until the complete disappearance of the starting material. The reaction was worked up by the addition of water and boiling for a couple of minutes and extracting the aqueous mixture with
methylene chloride. The combined organic layer was dried with anhydrous MgSO$_4$ and concentrated to give the unsubstituted sulfilimine. $^1$H-NMR (CDCl$_3$) $\delta$ 7.98(d, $J = 7.2$ Hz, 2H), 7.86 (d, $J = 6.9$ Hz, 2H), 7.60 (t, $J = 7.8$ Hz, 2H), 7.529 (t, $J = 7.5$ Hz, 2H).

**N-formyl dibenzothiophene sulfilimine, 1g.** Sulfilimine 1g was prepared by the addition of 1f to formic acetic anhydride. Formic acetic anhydride was prepared by heating acetic anhydride (0.341 mL) with 98% formic acid (0.168 mL) for two hours at 50-60°C in a flask fitted with a reflux condenser. After two hours, the solution was cooled to -50 °C. The solution of 1f (0.45g, 1.8 mmol) in methylene chloride was added slowly at -50°C and the reaction mixture was stirred at -50 °C and monitored for the disappearance of 1f. After complete disappearance, the solution was quenched with ice at -35 °C and the resulting solution was extracted quickly with ethyl acetate. The ethyl acetate layer was dried with MgSO$_4$ and concentrated to give the crude product. Tituration with hexane (to remove any DBT formed) gave pure 1g in ~30-35% yield. Care should be taken so that the temperature does not rise above -30°C due to decomposition of the product. $^1$H-NMR (CDCl$_3$) $\delta$ 7.98 (d, $J = 7.2$ Hz, 2H), 7.86 (d, $J = 6.9$ Hz, 2H), 7.60 (t, $J = 7.8$ Hz, 2H), 7.529 (t, $J = 7.5$ Hz, 2H).

**3.6 Acknowledgment**

We thank the National Science Foundation (Grant CHE-0211371) for support of this research.
3.7 References


(32) GCMS analysis indicated very small quantities of isomeric compounds, also of mass 281. These were interpreted as deriving from small isomeric impurities in the octene.


(46) It should also be noted that these are gas phase calculations. Polar solvents would presumably favor the singlet state by a few kcal/mol.

(47) The Mulliken bond orders are better behaved with modest basis sets such as 6-31G(d,p). There are other, more sophisticated models of bond order, but these values serve as very adequate comparative and qualitative guides.


CHAPTER 4

GENERAL CONCLUSIONS

In the previous chapters, the potential of dibenzothiophene-based sulfilimines as nitrene precursors was discussed. The results indicate that the dibenzothiophene moiety is an efficient platform for the generation of a variety of nitrenes (carbonyl, sulfonyl and the parent NH). The nature of the trapped products depends on the ground state multiplicity of the corresponding nitrenes generated.

Direct observation of singlet and triplet nitrene and phenyl isocyanate from the photolysis of N-benzoyl dibenzothiophene sulfilimine has been achieved by time-resolved IR. Oxygen and methanol quenching experiments in TRIR studies indicate that the singlet and triplet benzoylnitrene are distinct and are not rapidly equilibrating. Based on the time scale for decay of the singlet benzoyl nitrene and the growth of phenyl isocyanate, it is evident that the relaxed nitrenes are not responsible for the isocyanate. Indirect product studies provide additional insights into the mechanism. Wavelength dependant product studies indicate that phenyl isocyanate arises from the first excited state of the sulfilimine. The formation of primarily singlet-derived products implies that the decay of the singlet nitrene is the major reactive channel. Due to a paucity of triplet-derived products, we believe that the major pathway for triplet nitrene decay is its slow interconversion to the singlet ground state. The decreased quantum yields in oxygen-purged conditions in the product studies indicate likely quenching of the triplet-excited sulfilimine. This provides indirect evidence for S-N bond cleavage from the excited-triplet state of the sulfilimine.
The \( N \)-acetyl derivative was similar to the \( N \)-benzoyl counterpart in its photochemical behavior. TRIR experiments indicate equilibration of singlet and triplet acetylnitrene, although product studies are suggestive of decay via the singlet channel.

For the \( N \)-tosyl derivative, in spite of the lack of direct spectroscopic evidence, we were able to derive significant conclusions based on product studies. The lack of stereospecific formation of aziridines in octenes provides indirect evidence for triplet tosylnitrene. The significant decrease in the quantum yield of DBT under oxygen-purged photolysis and the increased quantum yield upon xanthone-sensitized photolysis indicate that the triplet nitrene is derived primarily from the triplet manifold, rather than intersystem crossing of singlet tosylnitrene. The formation of exiguous singlet nitrene-derived products substantiates the above inference. However, under high dilutions of a trapping agent or in the absence of a suitable H-donor, we observe singlet nitrene-derived products. Our most likely interpretation of this observed result is by considering an up-hill intersystem crossing of the triplet nitrene to the singlet state when other decay channels for the triplet are limited. Thus, we believe that the source of the singlet nitrene is the triplet nitrene, at least with regard to this precursor. We do not completely rule out the possibility of S-N bond cleavage from the excited-singlet state of the sulfilimine. Our results suggest that it would be a minor process compared to the S-N bond cleavage from the triplet manifold. The photochemistry contrasts with that of tosyl azide, in that the latter primarily yields singlet-derived products. The \( N \)-mesyl derivative follows the trend set by the \( N \)-tosyl derivative in yielding primarily triplet-derived products. Our calculations using B3LYP, MP2 and coupled-cluster methods predict a triplet ground state for mesynitrene with a \( \Delta E_{S-T} \) of \(~12\) kcal/mol. A stabilizing N-O bonding interaction exists in the \( C_1 \) symmetric singlet state of the nitrene. However, unlike
carbonylnitrenes, the bonding interaction is insufficient to change the ground state multiplicity to a singlet.

The trifluoroacetyl analogue yields mixed-stereochemistry aziridines indicating triplet nitrene reactivity. However, the trans/cis ratio of aziridines in cis-alkene was different from that obtained in trans-alkene suggesting the intermediacy of singlet nitrene, in addition to triplet. Our calculations using B3LYP and coupled-cluster methods indicate that the energy difference between the two spin-states of trifluoroacetylnitrene would be relatively smaller when compared to acetylnitrene. Therefore, we postulate a rapidly equilibrating singlet and triplet trifluoroacetylnitrene with the triplet being the ground state. Further work on establishing its ground state multiplicity is underway.

The efficiency of nitrene generation follows the order $N$-benzoyl $\sim N$-acetyl $> N$-tosyl $> N$-mesyl $\sim N$-trifluoroacetyl sulfilimine derivatives. All the sulfilimines analyzed show a potential for S-N bond cleavage from the excited triplet state of the sulfilimine. The results agree with our previously proposed mechanism for the photochemical unimolecular cleavage of DBTO leading to O($^3$P). The syntheses of $N$-formyl derivative and the unsubstituted parent dibenzothiophene sulfilimine open up avenues for the photochemical generation of formylnitrene and imidogen relatively easily.
## APPENDIX A

**Supporting Information for Chapter 2**

### Table of Contents

<table>
<thead>
<tr>
<th>Topic</th>
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<tbody>
<tr>
<td>Spectral data for synthesized compounds</td>
<td>135</td>
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<tr>
<td>Kinetic Traces for IR Data</td>
<td>140</td>
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<tr>
<td>Energies and Coordinates of Computed Structures</td>
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</tr>
<tr>
<td>Calculated Vibrational Frequencies</td>
<td>146</td>
</tr>
</tbody>
</table>
N-benzoylembenzothiophene sulfilimine (2)

(Prepared by Method A)
$^1$H NMR (400 MHz, CDCl$_3$)
Threeo $N$-benzoyl-2,3-di-n-propyl azidine (12a)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
Figure S1. Kinetic traces observed at (a) 1760 cm\textsuperscript{-1}, (b) 1635 cm\textsuperscript{-1} from -0.2 to 1.8 µs, and (c) 1635 cm\textsuperscript{-1} from -10 to 90 µs following 266 nm laser photolysis of sulfilimine 1 in argon-purged acetonitrile-\textit{d}_3. The dotted-line curves are experimental data and the solid lines are calculated best fits to a single-exponential function.
Figure S2. Kinetic traces observed at (a) 1760 and (b) 2265 cm$^{-1}$ following 266 nm laser photolysis of sulfilimine 1 (1 mM) in argon-purged dichloromethane. The dotted-line curves are experimental data and the solid lines are calculated best fits to a single-exponential function.
Figure S3. Kinetic traces observed at (a) 1616, (b) 1660, (c) 1504, and (d) 2265 cm\(^{-1}\) following 355 nm laser photolysis of xanthone (5 mM) in argon-saturated acetonitrile-\(d_3\). The dotted curves are experimental data; the solid curves are the calculated best fit to a single-exponential function.
Energies and Coordinates of Computed Structures

Table 1. Optimized geometry and energy for singlet benzoylnitrene $^1$.4.

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Table 2. Optimized geometry and energy for triplet benzoylnitrene $^3$4.

Theory: B3LYP/6-31G*

Zero-point correction= .101584 (Hartree/Particle)
Thermal correction to Energy= .108705
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Thermal correction to Gibbs Free Energy= .068475
Sum of electronic and zero-point Energies= -399.519307

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Table 3. Optimized geometry and energy for triplet excited state of azide 3.

Theory: B3LYP/6-31G*

Zero-point correction= .109550 (Hartree/Particle)
Thermal correction to Energy= .118943
Thermal correction to Enthalpy= .119887
Thermal correction to Gibbs Free Energy= .073317
Sum of electronic and zero-point Energies= -508.940923

Cartesian Coordinates:

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Calculated Vibrational Frequencies

**Table 4.** B3LYP/6-31G* calculated frequencies (cm\(^{-1}\), unscaled) and intensities for singlet benzoylnitrene \(^1\).4.

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Table 5. B3LYP/6-31G* calculated frequencies (cm\(^{-1}\), unscaled) and intensities for triplet benzoylnitrene \(^3\)A.

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Table 6. B3LYP/6-31G* calculated frequencies (cm\(^{-1}\), unscaled) and intensities for the lowest triplet excited state of benzoyl azide 3.

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**APPENDIX B**

**Supporting Information for Chapter 3**

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Spectral data for \( N \)-trifluoroacetyl dibenzothiophene sulfilimine, 1c
Spectral data for N-mesyl dibenzothiophene sulfilimine, 1d
Spectral data for N-Tosyl dibenzothiophene sulfilimine, 1e
Synthetic Preparations

Preparation of 6b

To (0.50 g 6.7 mmol) of acetohydroxamic acid in 4 mL methanol at -20 °C, was added NaH (0.15 g, 6.2 mmol) slowly with stirring. The resulting solution was gently stirred at room temperature for 20 minutes under argon and then refluxed for 4.5 hours. The resulting solution was cooled and then added isopropyl bromide (0.69 mL, 7.0 mmol) and refluxed overnight. After refluxing overnight, the solution was cooled and evaporated using a micro distillation kit. Product 6b crashed out and crude 1H-NMR indicates the presence of 6b. $^1$H-NMR (iPrOH-$d_8$) δ 1.26 (d, 6H, J = 7.8 Hz), 1.96 (s, 3H), 4.1 (m, 1H).
cis-3b: \(^1\)H-NMR (CDCl\(_3\)) \(\delta\) 0.9 – 1.01 (m, 6H), 1.42 – 1.62 (m, 6H), 1.7 – 1.8 (m, 2H), 2.40 – 2.45 (m, 2H), 2.02 (s, 3H). \(^{13}\)C-NMR (CDCl\(_3\)) \(\delta\) 13.9, 20.9, 21.2, 29.9, 41.5, 171.2

cis-3c. \(^1\)H-NMR (CDCl\(_3\)) \(\delta\) 0.9 – 1.05 (m, 6H), 1.35 – 1.45 (m, 6H), 1.50 – 1.62 (m, 2H), 2.70 – 2.80 (m, 2H). \(^{19}\)F-NMR (CDCl\(_3\)) \(\delta\) -73.92. \(^{13}\)C-NMR (benzene-d\(_6\)) \(\delta\) 13.1, 20.2, 25.7, 39.8, 162.4 (q, \(J = 34.8\) Hz), 117.5 (q, \(J = 290.8\) Hz).

cis-3d. \(^1\)H-NMR (CDCl\(_3\)) \(\delta\) 0.92 – 1.02 (m, 6H), 1.42 – 1.62 (m, 6H), 1.7 – 1.8 (m, 2H), 2.79 – 2.83 (m, 2H), 3.06 (s, 3H). \(^{13}\)C-NMR (benzene-d\(_6\)) \(\delta\) 13.1, 19.4, 28.7, 41.8, 44.1.

**Cartesian Coordinates of Computed Structures**

*Singlet acetylnitrene, \(^1\)2b*

B3LYP/6-31G(d,p)

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Triplet trifluoroacetyl nitrene $^2c$

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Singlet mesylnitrene, $^2d$

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**MP2/6-31G(d,p)**

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**Triplet mesylnitrene, \( ^1d \)**

**B3LYP/6-31G(d,p)**

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Halogenated Methane
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### B3LYP/6-31G(3d,p)

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### MCSCF(22,15)/6-31G(d,p)

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### MP2/6-31G(d,p) ROHF wavefunction

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### HF/6-31G(d,p) ROHF wavefunction

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**Cs-symmetric singlet mesylnitrene**

1^A" state GVB optimization

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S^1 A' state GVB optimization

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| C | 6.0 | 0.9216084124  | 0.0761886783 | 0.0000000000 |
| H | 1.0 | 1.2792192755  | -0.4167460102 | 0.8927209566 |
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MCSCF(22,14)/6-31G(d,p)

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| H | 1.0 | 1.2925808133  | -0.4104390110 | 0.8900298153 |
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**Singlet benzenesulfonylnitrene**

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### Energy Difference Calculations and Absolute Energies

**Table 1. Calculated electronic energies, Zero point energies (ZPE) and $\Delta H$ for CH$_3$CON**

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<th>Singlet CH$_3$CON</th>
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<td>H kcal/mol</td>
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Table 2. Calculated electronic energies, Zero point energies (ZPE) and ΔH for CF$_3$CON

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<td>B3LYP/b-311G(d,p)//B3LYP/6-31G(d,p)</td>
<td>-505.5341700</td>
<td>15.62406</td>
<td>20.145</td>
</tr>
<tr>
<td>B3LYP/6-311G(3df,2p) //B3LYP/6-31G(d,p)</td>
<td>-505.5232017</td>
<td>15.62406</td>
<td>20.145</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pVDZ/B3LYP/6-31G(d,p)</td>
<td>-505.4488245</td>
<td>15.62406</td>
<td>20.145</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pVTZ/B3LYP/6-31G(d,p)</td>
<td>-505.5797774</td>
<td>15.62406</td>
<td>20.145</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pWQZ/B3LYP/6-31G(d,p)</td>
<td>-506.6186849</td>
<td>15.62406</td>
<td>20.145</td>
</tr>
<tr>
<td>M06/6-31G(3df,2p)</td>
<td>-504.3676939</td>
<td>15.62406</td>
<td>20.145</td>
</tr>
<tr>
<td>M06-2X/6-31G(d,p)</td>
<td>-504.8619999</td>
<td>15.62406</td>
<td>20.145</td>
</tr>
<tr>
<td>OR-CCD(T)/6-311G(3df,2p) //B3LYP/6-31G(d,p)</td>
<td>-504.9384273</td>
<td>15.62406</td>
<td>20.145</td>
</tr>
<tr>
<td>M06-2X/6-31G(d,p)</td>
<td>-506.5769848</td>
<td>15.62406</td>
<td>20.145</td>
</tr>
<tr>
<td>M06-2X/6-31G(d,p)</td>
<td>-502.3751462</td>
<td>17.336504</td>
<td>21.63</td>
</tr>
</tbody>
</table>
### Table 3. Calculated electronic energies, Zero point energies (ZPE) and $\Delta H$ for CH$_3$SO$_2$N

<table>
<thead>
<tr>
<th>Method</th>
<th>Triplet CH$_3$SO$_2$N</th>
<th>Singlet CH$_3$SO$_2$N</th>
<th>$\Delta H$ (298 K) kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>-642.9234483 30.558524 34.72 11.754</td>
<td>-642.9024818 31.002286 35.037</td>
<td>13.037 14.1</td>
</tr>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>-642.9475758 30.532475 34.644 11.861</td>
<td>-642.9260734 31.88776 34.948</td>
<td>12.89 13.8</td>
</tr>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>-642.9711765 30.714657 34.77 12.105</td>
<td>-642.9495401 31.882923 35.098</td>
<td>13.125 14.0</td>
</tr>
<tr>
<td>B3LYP/6-31+G(d,p)/B3LYP/6-31G(d,p)</td>
<td>-643.0230614 30.558524 34.728 11.754</td>
<td>-643.0041910 31.002286 35.037</td>
<td>13.037 15.5</td>
</tr>
<tr>
<td>B3LYP/6-311G(d,f,2p)</td>
<td>-643.0873459 30.558524 34.728 11.754</td>
<td>-643.0677486 31.002286 35.037</td>
<td>13.037 12.6</td>
</tr>
<tr>
<td>B3LYP/cc-pVDZ/B3LYP/6-31G(d,p)</td>
<td>-642.9794790 30.558524 34.728 11.754</td>
<td>-642.9598024 31.002286 35.037</td>
<td>13.037 13.7</td>
</tr>
<tr>
<td>B3LYP/6-31G(d,p) //B3LYP/6-31G(d,p)</td>
<td>-643.1033457 30.558524 34.728 11.754</td>
<td>-643.0834934 31.002286 35.037</td>
<td>13.037 12.8</td>
</tr>
<tr>
<td>B3LYP/cc-pVQZ/B3LYP/6-31G(d,p)</td>
<td>-643.1208877 30.558524 34.728 11.754</td>
<td>-643.1102076 31.002286 35.037</td>
<td>13.037 12.7</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pVQZ/B3LYP/6-31G(d,p)</td>
<td>-643.0162801 30.558524 34.728 11.754</td>
<td>-643.0095045 31.002286 35.037</td>
<td>13.037 13.2</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pVTZ/B3LYP/6-31G(d,p)</td>
<td>-643.1094208 30.558524 34.728 11.754</td>
<td>-643.0909872 31.002286 35.037</td>
<td>13.037 12.6</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pVQZ/B3LYP/6-31G(d,p)</td>
<td>-643.1217114 30.558524 34.728 11.754</td>
<td>-643.1121487 31.002286 35.037</td>
<td>13.037 12.6</td>
</tr>
<tr>
<td>MP2/6-31G(d,p) //B3LYP/6-31G(d,p)</td>
<td>-641.8870184 31.708571 35.822 13.16</td>
<td>-641.8576663 32.17756 36.1</td>
<td>14.291 12.4</td>
</tr>
<tr>
<td>MP2/6-311G(d,f,2p) //B3LYP/6-31G(d,p)</td>
<td>-642.2600976 30.558524 34.728 11.754</td>
<td>-642.2525245 31.002286 35.037</td>
<td>13.037 5.1</td>
</tr>
<tr>
<td>MP2/aug-cc-pVTZ/B3LYP/6-31G(d,p)</td>
<td>-643.3083755 30.558524 34.728 11.754</td>
<td>-643.3019221 31.002286 35.037</td>
<td>13.037 4.4</td>
</tr>
<tr>
<td>MCQDT/6-31G(d,p) //MCF/32(15)/6-31G(d,p)</td>
<td>-641.9221991 32.823817 36.768 14.259</td>
<td>-641.8917678 32.821351 36.748</td>
<td>14.195 19.4</td>
</tr>
<tr>
<td>CR-CCSD(T)/6-311G(3df,2p) //B3LYP/6-31G(d,p)</td>
<td>-643.7967706 30.558524 34.728 11.754</td>
<td>-643.7637807 31.002286 35.037</td>
<td>13.037 17.2</td>
</tr>
<tr>
<td>CR-CCSD(T)/aug-cc-pVQZ //B3LYP/6-31G(d,p)</td>
<td>-643.1076512 30.558524 34.728 11.754</td>
<td>-643.0835843 31.002286 35.037</td>
<td>13.037 15.5</td>
</tr>
<tr>
<td>CR-CCSD(T)/G3Large* //B3LYP/6-31G(d,p)</td>
<td>-642.2846882 30.558524 34.728 11.754</td>
<td>-642.2647901 31.002286 35.037</td>
<td>13.037 12.8</td>
</tr>
</tbody>
</table>

### Table 4. Calculated electronic energies, Zero point energies (ZPE) and $\Delta H$ for PhSO$_2$N

<table>
<thead>
<tr>
<th>Method</th>
<th>Triplet PhSO$_2$N</th>
<th>Singlet PhSO$_2$N</th>
<th>$\Delta H$ (298 K) kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>-834.5413795 64.349286 70.091 41.762</td>
<td>-834.5193729 64.546224 70.444</td>
<td>43.251 14.5</td>
</tr>
<tr>
<td>B3LYP/6-311G(3df,2p) //B3LYP/6-31G(d,p)</td>
<td>-834.7628473 64.349286 70.091 41.762</td>
<td>-834.7479088 64.546224 70.444</td>
<td>43.251 15.1</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pVDZ/B3LYP/6-31G(d,p)</td>
<td>-834.6553895 64.349286 70.091 41.762</td>
<td>-834.6400555 64.546224 70.444</td>
<td>43.251 13.8</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pVTZ/B3LYP/6-31G(d,p)</td>
<td>-834.7909915 64.349286 70.091 41.762</td>
<td>-834.7706588 64.546224 70.444</td>
<td>43.251 13.2</td>
</tr>
<tr>
<td>MP2/6-31G(3df,2p) //B3LYP/6-31G(d,p)</td>
<td>-833.5852924 64.349286 70.091 41.762</td>
<td>-833.5576309 64.546224 70.444</td>
<td>43.251 4.1</td>
</tr>
</tbody>
</table>
Converged Active Spaces

*Singlet acetylnitrene '2b*
Active space used in MCSCF(6,5)/6-31G(d,p)

*Triplet acetylnitrene, '2b*
Active space used in MCSCF(6,5)/6-31G(d,p)
Singlet trifluoroacetylnitrene, $^12c$
Active space used in MCSCF(6,5)/6-31G(d,p)

Triplet trifluoroacetylnitrene, $^32c$
Active space used in MCSCF(6,5)/6-31G(d,p)
C1-symmetric singlet mesylnitrene
MCSCF(22,15)/6-31G(d,p) Active space
Cs-symmetric singlet mesylnitrene
Active space for MCSCF(22,15)/6-31G(d,p)
Cs-symmetric triplet mesynitrene
Active space for MCSCF(22,15)/6-31G(d,p) calculation