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Abstract

Photolysis of *N*-benzoyl-*S,S*-diphenylsulfilimine or *N*-benzoyl dibenzothiophene sulfilimine produces PhNCO and also benzoylnitrene. 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 time scale of a few microseconds and few tens of microseconds, respectively. Trapping experiments with substrates such as *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.

Disciplines

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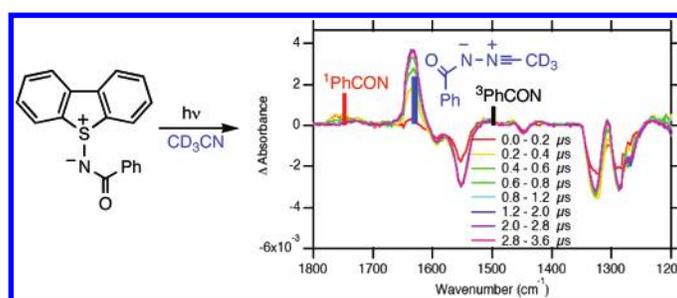
Photochemistry of Sulfilimine-Based Nitrene Precursors: Generation of Both Singlet and Triplet Benzoylnitrene

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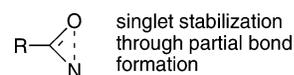
Photolysis of *N*-benzoyl-*S,S*-diphenylsulfilimine or *N*-benzoyl dibenzothiophene sulfilimine produces PhNCO and also benzoylnitrene. Direct observation of the triplet nitrene, energetic differences between the singlet and triplet state of the nitrene, and oxygen quenching experiments suggest that 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 time scale of a few microseconds and few tens of microseconds, respectively. Trapping experiments with substrates such as *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.

Introduction

Nitrenes are reactive intermediates that display a complex and fascinating chemistry that depends intimately on their multiplicity, mode of formation, and environment.^{1–6} Although most nitrenes have triplet ground states by substantial margins, aroylnitrenes generated from aroylazides have been notable in exhibiting primarily singlet reactivity.⁷ For example, acylnitrenes generated from the corresponding azide precursors have led to

stereospecifically trapped products, indicative of singlet nitrene reactivity.^{5,7}

Theoretical calculations and matrix isolation studies on acylnitrenes^{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 acetylnitrene using the CBS-QB3 method predict the ground state to be a singlet with $\Delta E_{S-T} = -4.9$ kcal/mol.⁹



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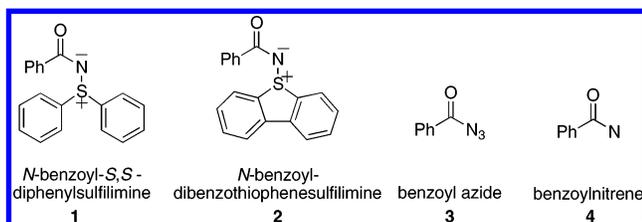
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Aroylazide precursors to aroylnitrenes are by far the most investigated; however, we believed that evidence accumulated in other investigations suggested that certain sulfilimines might also be excellent nitrene precursors. The photochemistry of dibenzothiophene-*S*-oxide (DBTO), which results in formation of dibenzothiophene, is well-documented.^{10–16} Numerous experiments support the formation of O(³P) as the major mechanism, though indirectly. (Other authors express skepticism.^{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.^{19,20} The dibenzothiophene (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 dibenzothiophene-based sulfilimines **1** and **2** are reported, along with a comparison to benzoylazide, **3**. In particular, we report the direct observation of ³4, which has not been experimentally demonstrated previously.



Results

1. Time-Resolved IR Studies. A. Direct Photolysis of 1 and 2. Upon 266 nm laser photolysis of *N*-benzoyl-*S,S*-diphenylsulfilimine **1** and *N*-benzoyl dibenzothiophene sulfilimine **2** in acetonitrile-*d*₃ (CD₃CN), 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

In CD₃CN, following the photolysis of either precursor (Figures 1 and 2), singlet benzoylnitrene (**4**) is observed at 1758 cm⁻¹, in good agreement with the singlet nitrene band observed

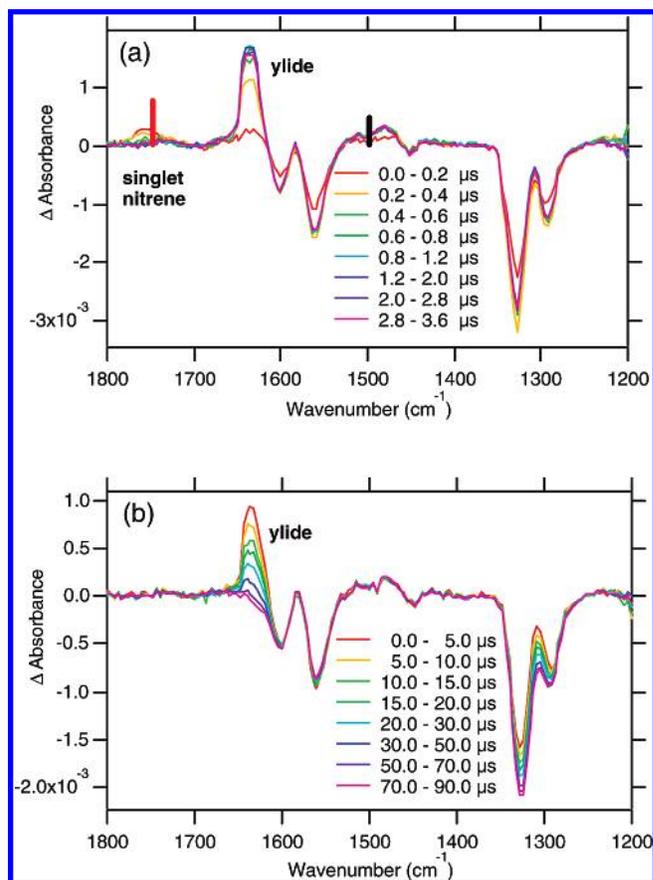
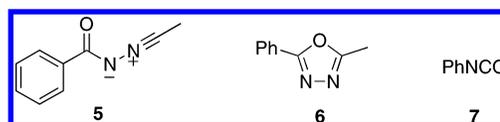


FIGURE 1. TRIR difference spectra (a) over 3.6 μs and (b) over 90 μs following 266 nm laser photolysis (5 ns, 2 mJ) of *N*-benzoyl-*S,S*-diphenyl sulfilimine **1** (1 mM) in argon-saturated CD₃CN, overlaid with bars representing B3LYP/6-31G(d) IR frequencies (scaled by 0.96) and relative intensities of singlet (red) and triplet (black) benzoylnitrene.

in the case of benzoylazide⁸ and the B3LYP/6-31G(d) calculated value (scaled by 0.96) of 1748 cm⁻¹.



From both precursors, bands attributed to the acetonitrile-*d*₃ ylide **5-d**₃ are observed at 1635 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 benzoylazide as the precursor.⁸ Over longer time scales (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**₃, in good agreement with the reported frequency of 1480 cm⁻¹.²² 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 Ph₂S.

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 at 1485 cm⁻¹ upon photolysis of **2** (Figure 3c). It has a similar

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(21) Kinetic traces obtained with **1** are shown in the Supporting Information.

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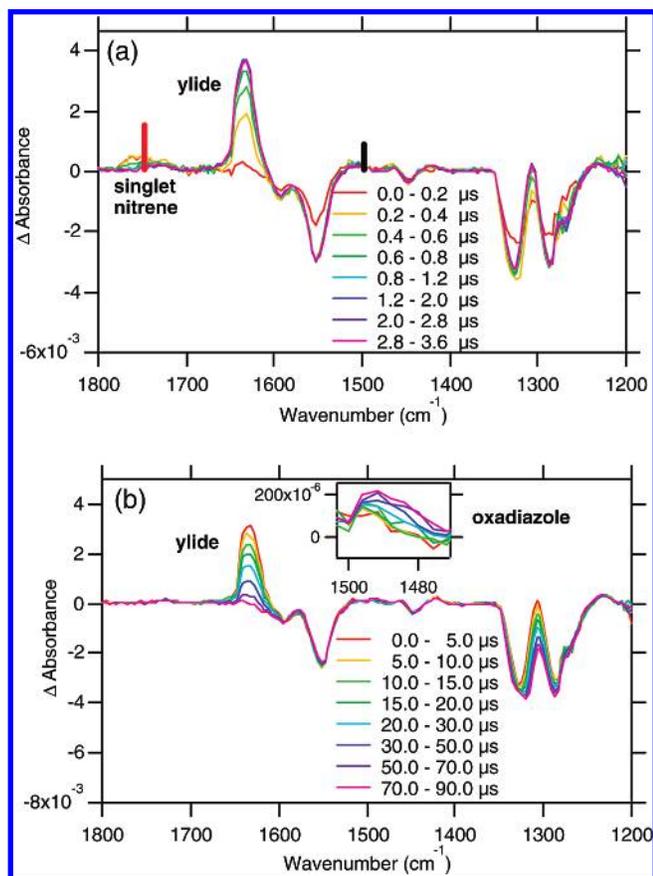


FIGURE 2. TRIR difference spectra averaged (a) over $3.6 \mu\text{s}$ and (b) over $90 \mu\text{s}$ following 266 nm laser photolysis (5 ns , 2 mJ) of **2** (1 mM) in argon-saturated CD_3CN , overlaid with bars representing B3LYP/6-31G(d) calculated IR frequencies (scaled by 0.96) and relative intensities of singlet (red) and triplet (black) benzoylnitrene.

lifetime (about $0.3 \mu\text{s}$) 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,³⁴ which has a calculated peak at 1497 cm^{-1} (scaled by 0.96).²³ The 1485 cm^{-1} peak is not observed after photolysis of **1**, due to the overlapping 1480 cm^{-1} absorption of Ph_2S .²⁴

On photolysis of **2** in dichloromethane, the singlet benzoylnitrene peak at 1758 cm^{-1} ($k_{\text{obs}} = 6.0 \times 10^5 \text{ s}^{-1}$, Figures 5 and 6a) is observed, along with a peak assigned to phenylisocyanate, **7**, 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} Additionally, the observed lifetimes of singlet benzoylnitrene depend on the precursor in dichloromethane solvent: about $2 \mu\text{s}$ for the sulfur-based precursors **1** and **2**, and about $6 \mu\text{s}$ for benzoyl azide.

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(24) Other DBT-based sulfilmines 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.

The triplet nitrene band at 1485 cm^{-1} band is also observed (Figure 5). It decays with a time constant of $1.8 \times 10^6 \text{ s}^{-1}$. 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 $^1\text{2}^*$ to form $^3\text{2}^*$ 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 arylnitrenes, however, react sluggishly with O_2 , with rate constants typically near $10^5 \text{ M}^{-1} \text{ s}^{-1}$.^{26–30} In contrast, benzoylnitrene and triplet carbenes react with O_2 at rate constants much closer to $10^9 \text{ M}^{-1} \text{ s}^{-1}$,^{31–34} which is the order of magnitude required for rapid suppression of the benzoylnitrene 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.

B. Triplet-Sensitized Photolysis of Benzoylazide. In previous work, some of us have demonstrated that singlet nitrene could be observed by IR from direct photolysis of benzoylazide.⁸ However, no triplet nitrene was observed. For comparison to the data from **2**, then, we examined the xanthone-sensitized photochemistry of benzoylazide, 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.

The spectrum in Figure 8a was recorded after 355 nm photolysis of xanthone (5 mM) in CD_3CN . After rapid intersystem crossing, the triplet state of xanthone ($^3\text{X}^*$) decays back to ground state with a first-order rate constant of $2.8 \times 10^6 \text{ s}^{-1}$ (Supporting Information). The spectrum in Figure 8b was recorded after 355 nm excitation of a similar solution with 20 mM benzoylazide 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 $^3\text{X}^*$ is significantly reduced.³⁵ The ylide IR band at 1636 cm^{-1} ($k_{\text{growth}} = 3.6 \times 10^6 \text{ s}^{-1}$, $k_{\text{decay}} = 3.7 \times 10^4 \text{ s}^{-1}$) is still observed and may be compared to data obtained from direct photolysis of benzoylazide ($k_{\text{growth}} = 3.4 \times 10^6 \text{ s}^{-1}$ and $k_{\text{decay}} = 4.1 \times 10^4 \text{ s}^{-1}$).⁸

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

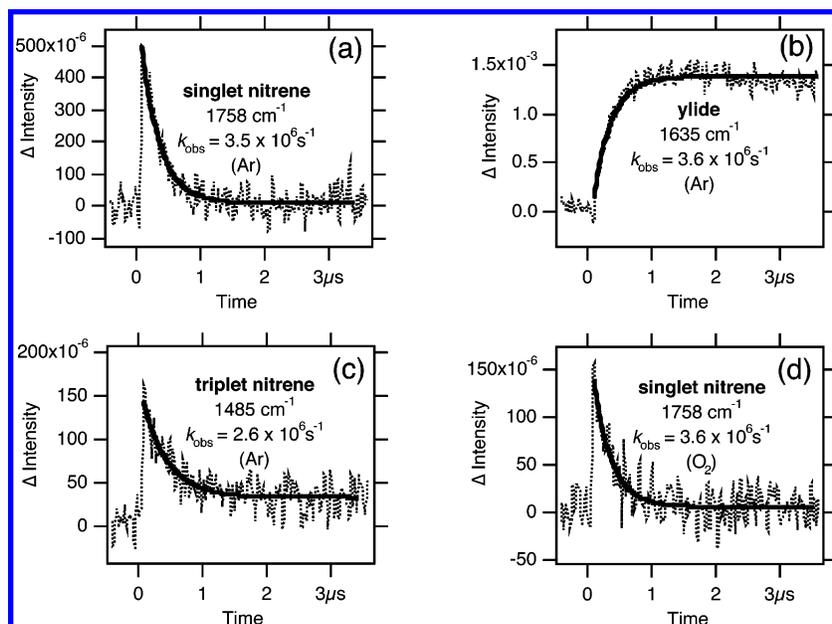


FIGURE 3. Kinetic traces observed at (a) 1758 , (b) 1635 , and (c) 1485 cm^{-1} following 266 nm laser photolysis (5 ns , 2 mJ) of **2** (1 mM) in argon-saturated acetonitrile- d_3 and at (d) 1758 cm^{-1} in oxygen-saturated CD_3CN . The dotted curves are experimental data; the solid curves are the calculated best fit to a single-exponential function.

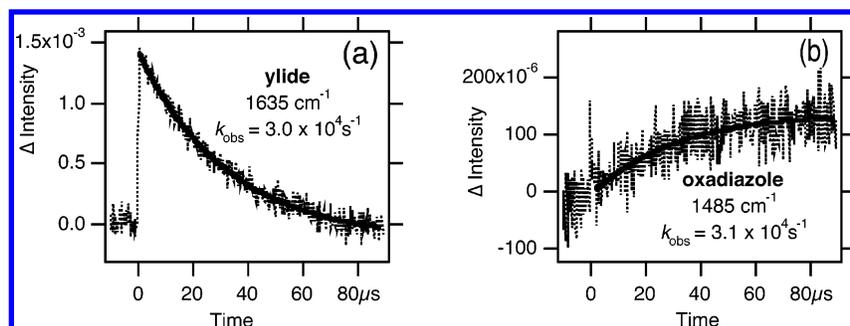


FIGURE 4. Kinetic traces observed at (a) 1635 and (b) 1485 cm^{-1} following 266 nm laser photolysis (5 ns , 2 mJ) of **2** (1 mM) in argon-saturated CD_3CN . The dotted curves are experimental data; the solid curves are the calculated best fit to a single-exponential function.

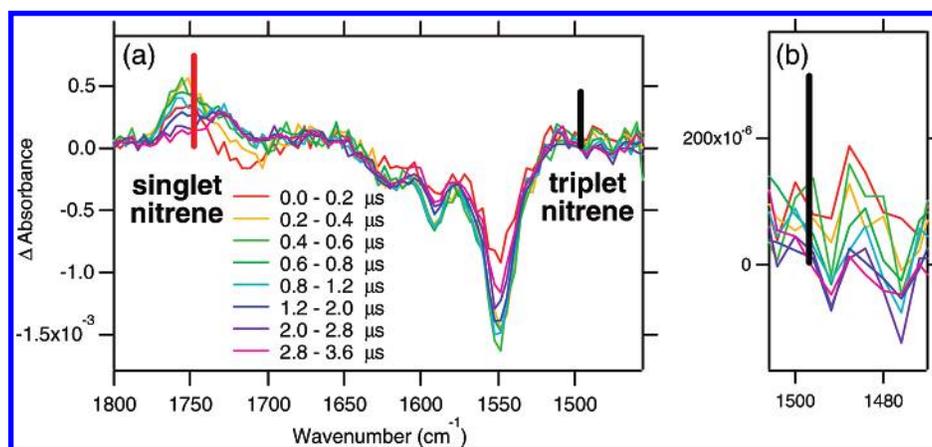


FIGURE 5. TRIR difference spectra averaged over the time scales indicated following 266 nm laser photolysis (5 ns , 2 mJ) of *N*-benzoyl dibenzothiophenesulfilimine **2** (1 mM) in argon-saturated dichloromethane (a) between 1800 and 1465 cm^{-1} and (b) an enlarged view between 1520 and 1470 cm^{-1} , 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.

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 the triplet excited state of

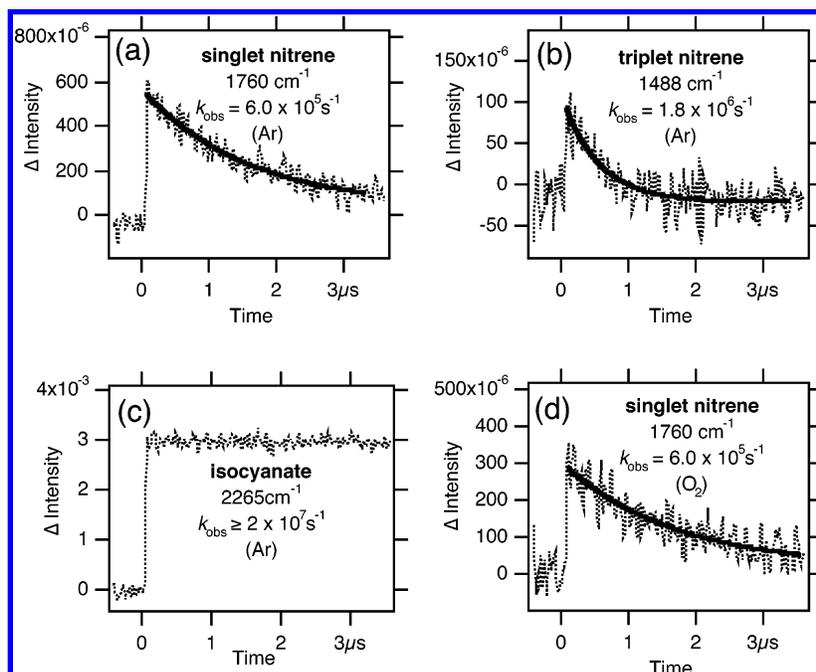


FIGURE 6. Kinetic traces observed at (a) 1760, (b) 1488, and (c) 2265 cm^{-1} following 266 nm laser photolysis (5 ns, 2 mJ) of *N*-benzoyl dibenzothiophenesulfilimine **2** (1 mM) in argon-saturated dichloromethane and at 1760 cm^{-1} in oxygen-saturated dichloromethane. The dotted curves are experimental data; the solid curves are the calculated best fit to a single-exponential function.

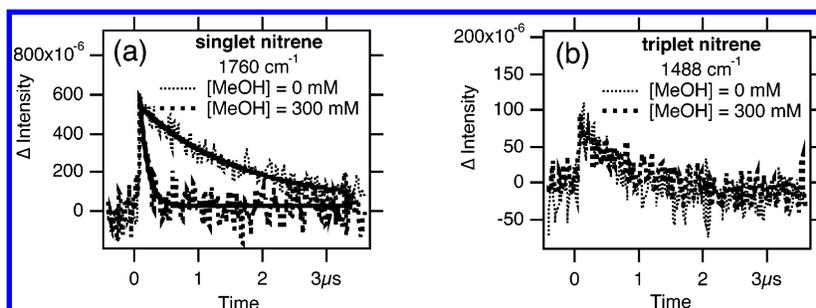


FIGURE 7. The trapping reactions of nitrenes with methanol observed at (a) 1760 and (b) 1488 cm^{-1} following 266 nm laser photolysis (5 ns, 2 mJ) of *N*-benzoyl dibenzothiophenesulfilimine **2** (1 mM) in acetonitrile- d_3 . The dotted curves are experimental data; the solid curves are the calculated best fit to a single-exponential function.

benzoylazide; 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 benzoylazide 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 the 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 benzoylazide.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.

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

2. 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 ($\leq 15\%$), 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 CH_3OH and *i*PrOH, and the

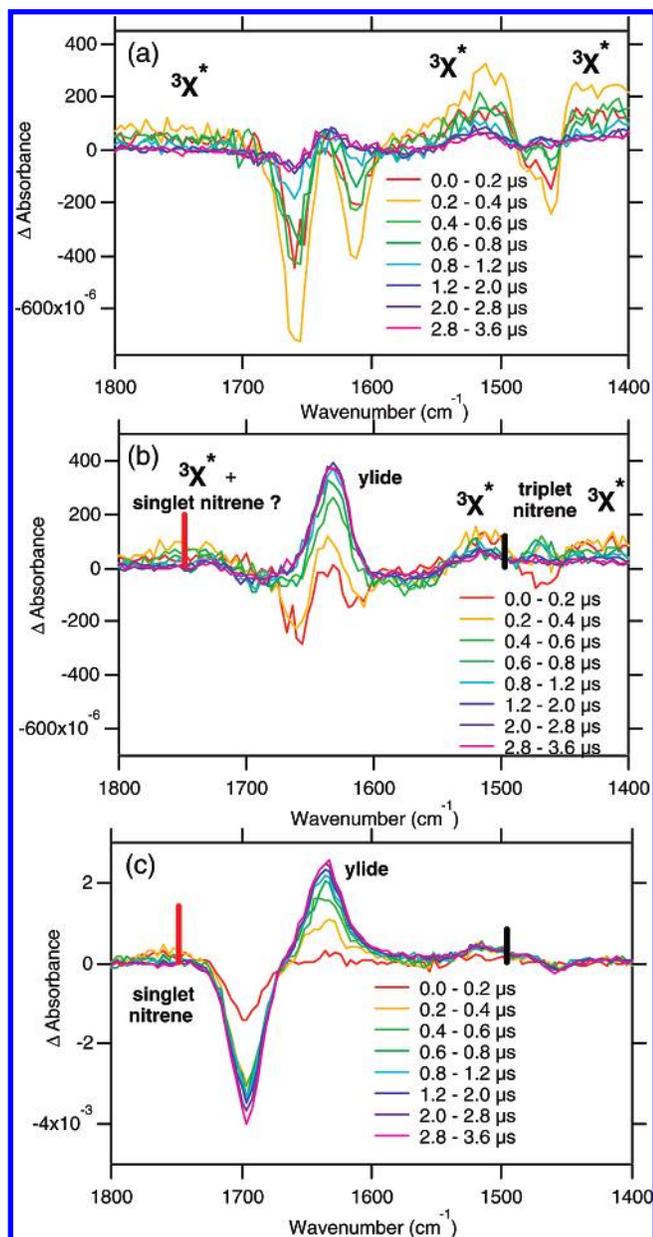
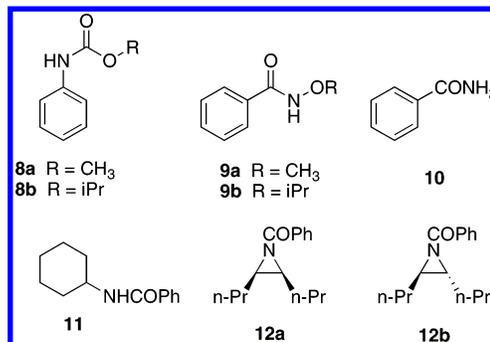


FIGURE 8. TRIR difference spectra averaged over the time scales indicated, following 355 nm laser photolysis (5 ns, 2 mJ) of (a) xanthone (5 mM) and (b) benzoylazide with xanthone (20 mM/5 mM), and (c) following 266 nm laser photolysis of benzoylazide in argon-saturated acetonitrile- d_3 . $^3X^*$: triplet 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.

appropriate carbamates **8a** and **8b** were observed in modest yields (e.g., entries 1–4).³⁷ The *N*-alkoxybenzamides **9a** and **9b** were taken as singlet nitrene quenching products under the same conditions, arising from OH insertion by the nitrene.^{38,39} 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.



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_2Cl_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 versus 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 benzoylnitrene (**14**) and the alkene and the alternate possibilities of a reaction between the ylide **5** or **2*** and the alkenes. (Since **12a** 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 (**34**) 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 naphthoynitrene.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

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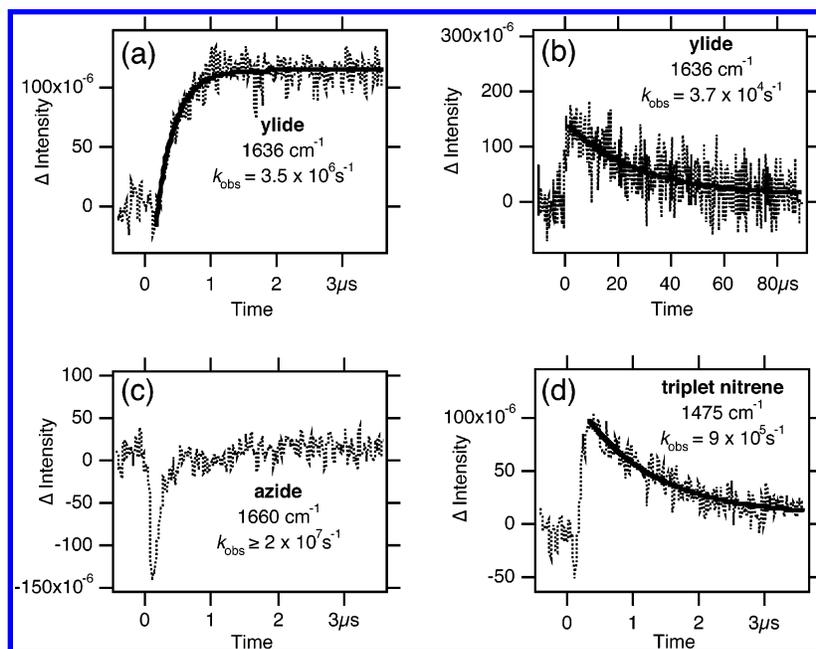


FIGURE 9. Kinetic traces observed at (a and b) 1636, (c) 1660, and (d) 1475 cm^{-1} following triplet-sensitized photolysis (355 nm, 5 ns, 2 mJ) of benzoylazide (20 mM, $A_{355} = 0$) using xanthone (5 mM, $A_{355} = 0.3$) in argon-saturated acetonitrile- d_3 . The dotted curves are experimental data; the solid curves are the calculated best fit to a single-exponential function.

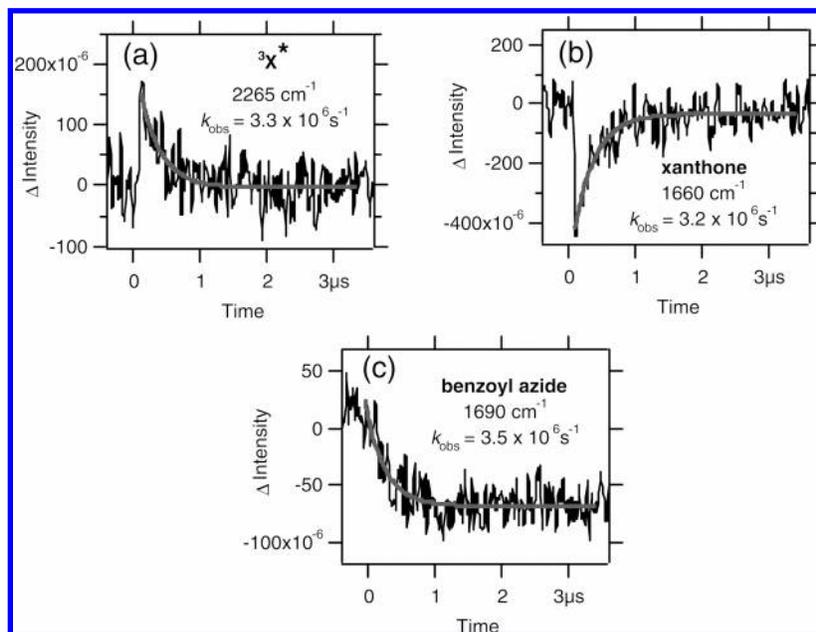


FIGURE 10. Kinetic traces observed at (a) 2265, (b) 1660, and (c) 1690 cm^{-1} following triplet-sensitized photolysis (355 nm, 5 ns, 2 mJ) of benzoylazide (5 mM, $A_{355} = 0$) using xanthone (5 mM, $A_{355} = 0.3$) in argon-saturated dichloromethane. The dotted curves are experimental data; the solid curves are the calculated best fit to a single-exponential function.

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_2Cl_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 versus the nitrene (compare entries 13–15 to entries 1 and 2), but there were no new products, nor products that were excluded. This is in contrast to benzoylazide as a precursor to benzoylnitrene,

TABLE 1. Product Yields on Photolysis of **2**

entry	solvent	λ , nm	Φ_{DBT}	purge	product yields (%), relative to DBT					
					6	8a/b ^c	9a/b ^c	10	11	12a/b
1	CH ₃ OH ^a	320	0.49	Ar		17	80	trace		
2	CH ₃ OH ^a	320	0.36	O ₂		34	64	trace		
3	<i>i</i> PrOH ^a	320	0.83	Ar		18	80	4		
4	<i>i</i> PrOH ^a	320	0.56	O ₂		35	61	4		
5	10% cyclohexane in CH ₃ CN ^b	320	1.0	Ar	52				5	
6	50% cyclohexane in CH ₂ Cl ₂ ^b	320	0.72	Ar					71	
7	10% <i>cis</i> -octene in CH ₃ CN ^a	320	0.76	Ar	9					72/0 ^d
8	10% <i>trans</i> -octene in CH ₃ CN ^a	320	0.81	Ar	22					0/44 ^d
9	CD ₃ OD ^{a,b}	350 X ^e		Ar			100			
10	<i>i</i> PrOH ^b	350 X ^e		Ar			20	43		
11	50% cyclohexane in CH ₂ Cl ₂ ^b	350 X ^e	0.65	Ar				39	49	
12	10% cyclohexane in CH ₃ CN ^b	350 X ^e	0.67	Ar	63			5	6	
13	CH ₃ OH ^a	365		Ar		35	60	trace		
14	CH ₃ OH ^a	365		O ₂		41	58	trace		
15	CH ₃ OH ^a	355		Ar		35	60	trace		

^a Product yields determined by ¹H NMR integration after complete conversion of starting material. ^b Product yields determined by GC-MS after complete conversion of starting material. ^c Methyl (a) or isopropyl (b) derivatives were observed, as appropriate. ^d Complete retention of stereochemistry from olefin to aziridine was observed. ^e Xanthone as sensitizer, ca. 4 mM.

in that the azide is thought only to produce phenylisocyanate from an upper excited state.⁷

For comparison, direct photolysis of benzoylazide in *i*PrOH (compare to entry 3 of Table 1) produced 2% benzamide, 53% **8b**, and 48% **9b**, relative to consumed benzoylazide. 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 aroylazide, but rather begins with hydrogen abstraction from *i*PrOH by xanthone.^{7,45}

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 alkylnitrenes 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 analogues.⁴⁶ Finally, again appealing to the sulfoxide photochemistry analogue, the photochemistry of diphenyl sulfoxide⁴⁷ is known to be more complex than that of dibenzothiophene.^{11,48}

A comment on sulfoxide deoxygenation chemistry is also in order with the results of this paper. Although extensive *indirect*

evidence has existed that the mechanism is a unimolecular dissociation to form atomic oxygen O(³P) 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 benzoylazide. 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⁻¹ cm⁻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 (Sul-

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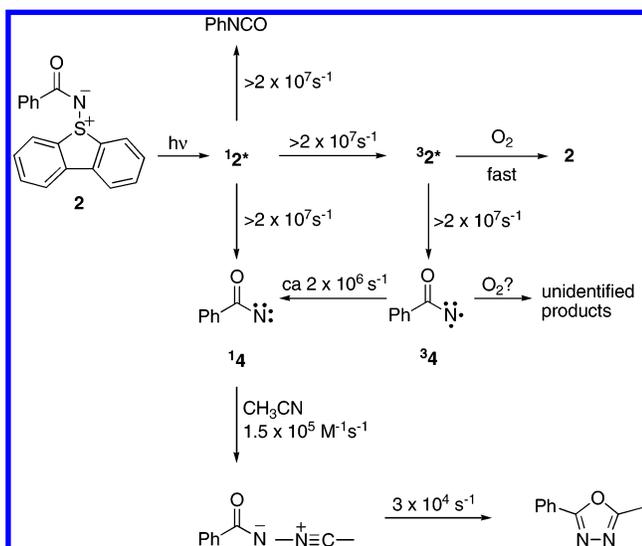
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SCHEME 1



foxidic 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 time scale 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 aroylazide photochemistry, Schuster reported a wavelength dependence that showed that an upper excited state was the precursor to the isocyanate, in that red-edge photolysis provided only nitrene-derived products.⁷ 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, Gudmundsdottir recently demonstrated a competition between α -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 benzoylazide, based on the peak at 1758 cm^{-1} .⁸ The appearance of this peak is instantaneous on this time scale. The decay time constant is about the same for **1** and for **2** as precursors. In dichloromethane, this decay time is about 3 times faster than that recorded for benzoylazide 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 14 .⁵² In acetonitrile, the lifetime of the singlet nitrene is shorter, and does not vary with precursor; this is attributable to the greater facility with which acetonitrile reacts with the nitrene.

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 $30 \mu\text{s}$. 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 6-fold 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 shows that there is not rapid interconversion between the two spin states of the benzoylnitrene, 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 32 or 34 , 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 **8a** and **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, **10**, which is generally observed in only small amounts (Table 1). Previous workers have demonstrated that excited triplet aroylazides may react with cyclohexane to give part of the yield of benzamides observed on photolysis of benzoylazide and its analogues.⁷ We cannot rule out some analogous reaction of 32 , though it seems less likely than in the case of the aroylazides, 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 $< 10^6 \text{ M}^{-1} \text{ s}^{-1}$, assuming the first step of C–N bond formation is irreversible. This is also an expected result.^{7,53}

Because not all the mass balances are excellent, we considered other possible products. Gudmundsdottir has recently shown that triplet alkylnitrenes dimerize and yield products derived from their photolytic loss of N_2 in a secondary reaction.^{54–56} The illustrated expected analogue would yield benzaldehyde; no

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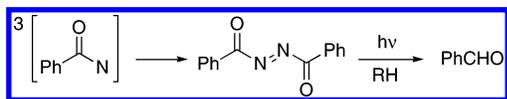
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evidence of that product has been obtained.



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

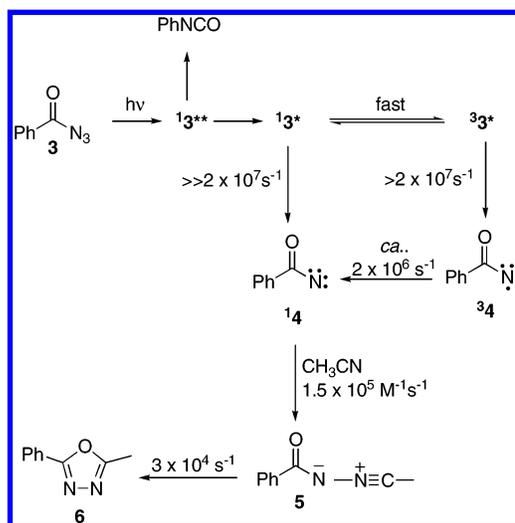
The insertion of the nitrene into cyclohexane is a product that can be attributed, in principle, to either singlet or triplet chemistry. Elegant experiments by Hall and co-workers explicitly argued for the partial intervention of triplet phenylnitrene in certain C–H insertions,⁵⁸ though others have argued such insertions were due to singlet chemistry in cases closely related to ours.^{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, O₂ 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 O₂ may additionally quench ¹2* because of the large energy gap between ¹2* and ³2*. Addition of O₂ 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 lost 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% CH₃CN. 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

SCHEME 2



*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 benzoylazide, 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 time scale that is inconsistent with formation of the singlet nitrene via slow intersystem crossing 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 ¹PhCON₃ 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.⁷ 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.^{7,45}

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 nitrenes are observed directly. Shorter nitrene lifetimes with **1** or **2** than when benzoylazide is used as a precursor in dichloromethane suggest that back reaction with the sulfide may be a significant process. Triplet benzoylnitrene, although not the ground state

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of the nitrene, still disappears only on the microsecond time scale. 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 $^1\text{2}^*$ 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.

Experimental Section

Time-Resolved IR Methods. The TRIR experiments have been conducted following the method of Hamaguchi and co-workers^{59,60} as has been described previously.⁶¹ Briefly, the broadband output of a MoSi₂ IR source is crossed with excitation pulses from either a Q-switched Nd:YAG laser (266 nm, 90 ns, 0.4 mJ) operating at 200 Hz or a 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, amplified, digitized with an oscilloscope, and collected for data processing. The experiment is conducted in dispersive mode.

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 75 W xenon Arc lamp fitted to a monochromator set to the specified wavelength with ± 12 nm linear dispersion. Valerophenone was used as the actinometer,⁶⁶ 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 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 ¹H 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 ¹H NMR was relied upon.^{67,68} The ¹H NMR spectrum of the analogue 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**,⁶⁹ benzoylazide **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: ¹H NMR (CDCl₃) δ 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); ¹³C NMR (CDCl₃) δ 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 ¹H 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 CH₂Cl₂ at –78 °C was added dibenzothiophene-*S*-oxide¹¹ (0.5 g, 2.5 mmol) in CH₂Cl₂. 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 to room temperature. The reaction mixture was washed with saturated sodium bicarbonate, and the organic layer was dried and concentrated to give the crude product. Purification was by silica chromatography using 5% EtOAc in CH₂Cl₂ as eluent to give **2** in 30% yield: ¹H NMR (CDCl₃) δ 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); ¹³C NMR (CDCl₃) δ 122.3, 127.9, 128.9, 129.0, 129.9, 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:** *N-p*-Tosyldibenzothiophene sulfilimine was made following the known literature procedure for related compounds.⁷⁵ *N-p*-Tosyldibenzothiophene sulfilimine (1.0 g, 2.8 mmol) was dissolved in 10 mL of concentrated sulfuric acid (95%) at room temperature for about 2 h, and the resulting solution was then poured into 100 mL of cold diethyl ether. After removal of the ether, the oily mixture was dissolved in 100 mL of chloroform, washed with ammonium hydroxide (2 \times), followed by water (5 \times), dried with sodium sulfate, and the solvent was removed. The white solid was then dissolved in 50 mL of benzene and 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 of dichloromethane, washed with water (5 \times), dried with sodium sulfate, and the solvent was removed.

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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.

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Supporting Information Available: Spectral data on new compounds, additional TRIR data, and documentation of all computational data are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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