

# Laser Flash Photolysis Studies of Oxygen and Sulfur Atom Transfer Reactions from Oxiranes and Thiiranes to Singlet Carbenes<sup>1</sup>

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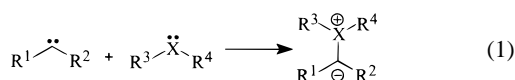
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**Abstract:** Laser flash photolysis (UV-LFP) studies of benzylchlorodiazirine (**1a**), phenylchlorodiazirine (**1b**), phenylmethoxydiazirine (**1c**), 2,2-dimethoxy-5,5-dimethyl- $\Delta^3$ -1,3,4-oxadiazoline (**6a**), 3,4-diaza-2,2-dimethoxy-1-oxa[4.3]spirooct-3-ene (**6b**), 5',5'-dimethoxyspiro[adamantane]-2,2'-[ $\Delta^3$ -1,3,4-oxadiazoline] (**6c**), and diazofluorene (**DAF**) in the presence of oxiranes and thiiranes are reported. These compounds, upon irradiation, afford benzylchlorocarbene (**2a**), phenylchlorocarbene (**2b**), methoxyphenylcarbene (**2c**), dimethylcarbene (**8a**), cyclobutylidene (**8b**), adamantylidene (**8c**), and fluorenylidene (**FL**), respectively. Absolute rate constants for the transfer of oxygen and sulfur atoms to these carbenes have been determined in both acetonitrile and cyclohexane solvents. These carbenes abstract oxygen and sulfur atoms with bimolecular rate constants ranging from  $10^4$  to  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  at 22 °C. Ylides from attack of carbenes onto heteroatom donors were not observed for any of the heteroatom transfer reactions. It was found that the magnitudes of the rate constants for heteroatom transfer are dependent on the *philicity* of the carbene intermediate, and trends in the kinetic data suggest that oxygen and sulfur atom transfers occur by concerted mechanisms through ylide-like transition states. The reactions of dimethoxycarbene (**14**) with cyclohexene oxide and propylene sulfide have been studied by the thermolysis of **6a**, in benzene, at 110 °C. It was found that dimethoxycarbene also abstracts oxygen and sulfur atoms, albeit in low yields. It is concluded that, for singlet carbenes, carbene electrophilicity is important in these heteroatom transfer processes.

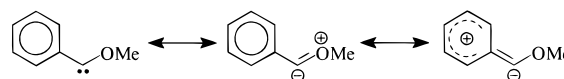
## Introduction

It is well-known that electrophilic singlet carbenes interact with lone pairs of electrons of heteroatoms to form ylide intermediates, eq 1, as do electrophilic transition metal carbeneoids.<sup>2</sup> An understanding of the ylide-forming abilities of carbenes is of fundamental importance in terms of their use in synthesis,<sup>2</sup> and for formulating mechanistic rationales for new reactions of carbenes with reactants containing heteroatoms.



Ylide-forming reactions have been used extensively for determining inter- and intramolecular reactivity of carbenes that do not have absorptions in useful regions of the UV–vis

spectrum.<sup>3,4</sup> Ylides derived from pyridine have been employed in this fashion and it has been shown that carbenes of different structure react with pyridine with rate constants ranging from  $10^5$  to  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>5</sup> Carbenes such as oxycarbenes, which bear one or two  $\pi$ -donor substituents and are ambiphilic or nucleophilic in character,<sup>6</sup> have been shown to react with pyridine up to 5 orders of magnitude more slowly than electrophilic carbenes, such as those with alkyl or halogen substituents.<sup>5,7,8</sup> For example, methoxyphenylcarbene, which contains two  $\pi$ -donor substituents and is considered to be an ambiphilic carbene with a large degree of nucleophilic character ( $m_{\text{CXY}}^{\text{calcd}} = 1.34$ ),<sup>9</sup> reacts with pyridine with a bimolecular rate constant of  $k_{\text{pyr}} = 1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , whereas phenylchlorocarbene, which is a more electrophilic ambiphile by comparison ( $m_{\text{CXY}}^{\text{calcd}} = 0.71$ ),<sup>4a,6a,b,8,10</sup> reacts with pyridine with a rate constant of  $k_{\text{pyr}} = 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  in hydrocarbon solvent at ambient temperatures.<sup>8</sup>



Electrophilic carbenes such as dialkylcarbenes<sup>11</sup> ( $m_{\text{CXY}} \approx 0.2$ ), dimethylcarbene has an  $m_{\text{CXY}}^{\text{calcd}} = 0.19$ ) and chlorocarbene<sup>12</sup> ( $m_{\text{CXY}}^{\text{calcd}} = 0.46$ ) react with pyridine with rate constants at or

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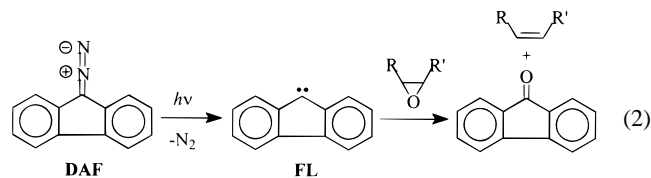
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near the diffusion controlled limit;  $k_{\text{pyr}} = (1-8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Dialkylcarbenes tend to show electrophilic singlet state chemistry,<sup>3,4</sup> and intramolecular 1,2-hydrogen shifts are usually dominant for these intermediates. Exceptions include carbenes without  $\alpha$ -hydrogens as exemplified by di(1-adamantylcarbene).<sup>13</sup> In singlet alkyl and dialkylcarbenes those shifts involve transition states in which the migrating atom is hydride-like.<sup>3,4</sup> The electrophilic character of such carbenes<sup>3,4</sup> is also indicated by their preference for electron-rich olefins in cyclopropanation reactions and by their rapid reactions with substrates containing heteroatoms, such as pyridine.<sup>3,4d-f</sup> The rapid (close to the diffusion-controlled limit) formation of pyridine ylide intermediates from singlet dialkylcarbenes suggests that reactions of these carbenes with heteroatom donors could successfully compete with intramolecular rearrangement reactions.

Electrophilic singlet carbenes are capable of abstracting oxygen and sulfur atoms by mechanisms involving the formation of ylide intermediates (or ylide-like transition states), followed by heteroatom transfer. Some examples include heteroatom

abstraction from  $\text{CO}_2$ ,<sup>14</sup>  $N$ -oxides,<sup>15</sup>  $\text{PF}_3\text{O}$ ,<sup>16</sup> epoxides,<sup>17</sup> aziridines,<sup>18</sup> thiiranes,<sup>19</sup> and carbonyl compounds.<sup>20</sup> Shields and Schuster have shown that oxygen atom abstraction from epoxides by singlet fluorenylidene (FL) occurs stereospecifically (eq 2).<sup>17a</sup>



Reaction of carboethoxycarbene with styrene oxide leads to deoxygenation products as well as a diastereomeric mixture of oxetanes,<sup>17c</sup> presumably resulting from the intramolecular rearrangement of an oxonium ylide intermediate. Carboethoxycarbene has also been shown to abstract the sulfur atom from cyclohexene sulfide without similar intramolecular rearrangement.<sup>19</sup>

Herein we report heteroatom transfer reactions from oxiranes and thiiranes to a variety of carbenes of different structure and philicity ( $m_{\text{CXY}}$ ). We have explored the heteroatom transfer chemistry of benzylchlorocarbene (**2a**),<sup>21-24</sup> phenylchlorocarbene (**2b**),<sup>10</sup> and methoxyphenylcarbene (**2c**),<sup>9b</sup> all of which have singlet ground states and are ambiphilic. These carbenes were generated from the photolysis of the corresponding diazirine precursors (**1a-c**). Oxadiazoline precursors were used to study heteroatom transfer reactions of dimethylcarbene (**8a**), cyclobu-

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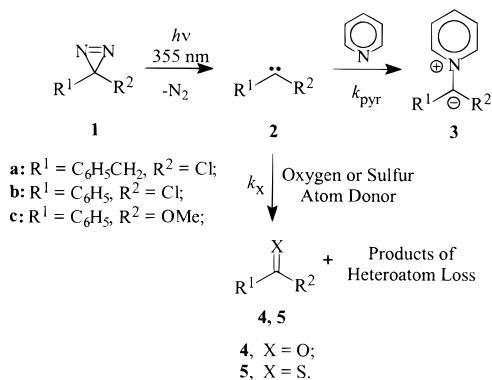
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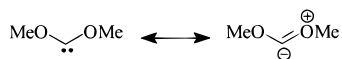
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## Scheme 1



tylidene (**8b**), and 2-adamantylidene (**8c**) with oxiranes and thiiranes. LFP studies of oxadiazoline precursors by time-resolved infrared detection (TRIR) have demonstrated the formation of diazoalkanes.<sup>25</sup> Dialkylcarbenes,<sup>26</sup> possibly formed via a multiphoton absorption by these precursors in the laser beam, are also generated. Diazofluorene (DAF) was also employed here to study the atom transfer chemistry between propylene sulfide and fluorenylidene (FL). Rate constants for heteroatom transfer reactions between heteroatom donors and carbenes **2**, **8a–c**, and FL were determined by laser flash photolysis (LFP).

In contrast to the photochemical reaction of 2,2-dimethoxy-5,5-dimethyl-Δ<sup>3</sup>-1,3,4-oxadiazoline (**6a**), thermal decomposition of **6a** leads to the formation of dimethoxycarbene.<sup>27</sup> The latter is stabilized by conjugative donation by the lone pairs on oxygen to the formally vacant p-orbital at the carbene carbon.<sup>28,29</sup> As a result, dimethoxycarbene has dipolar character and acts as a nucleophile.



This conjugative donation strongly stabilizes the singlet state, and the singlet/triplet energy gap has been calculated to be ~76 kcal/mol.<sup>29</sup> Inclusion of dimethoxycarbene in the present study expands the range of carbene reactivities to include electrophilic, ambiphilic, and archetypal nucleophilic carbenes ( $m_{\text{CX}}$  varying between ~0.2 and 2.22).

## Results

**Determination of Rate Constants for Carbene Reactions with Heteroatom Donors by Laser Flash Photolysis. (a) Benzylchlorocarbene.** Absolute rate constants for the reaction of benzylchlorocarbene (**2a**) with oxygen and sulfur atom donors were measured by means of UV-LFP and the pyridine ylide probe method<sup>3,4</sup> (Scheme 1). Upon irradiation of 3-benzyl-3-chlorodiazirine (**1a**) (355 nm, 10 ns pulse, 40 mJ) in the presence

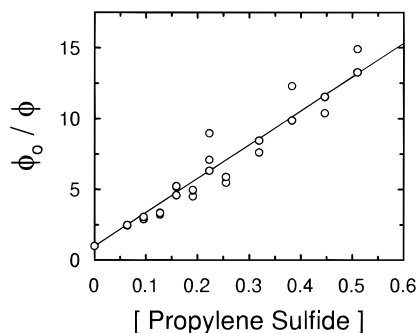
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**Figure 1.** Stern-Volmer quenching plot for the reaction of propylene sulfide with benzylchlorocarbene in cyclohexane at 22 °C.

of pyridine, a long-lived (stable on the  $\mu\text{s}$ – $\text{ms}$  time scale) absorption centered at  $\lambda \approx 370$  nm, previously assigned to the pyridinium ylide **3a**, was observed.<sup>4g,22a,c</sup> It was found that the intensity of this absorption was inversely proportional to the concentration of heteroatom donor, with constant diazirine and pyridine concentrations.

The ratios  $k_X/k_{\text{pyr}}$  [pyridine], where  $k_X$  are the bimolecular rate constants for the reactions of benzylchlorocarbene (**2a**) with heteroatom donor traps, and  $k_{\text{pyr}}$  is the bimolecular rate constant for the reaction of **2a** with pyridine, were determined by linear least-squares analysis of the ratio ( $A^{\circ}_{\text{ylide}}/A_{\text{ylide}}$ ) versus trap concentration, with the y-intercept defined as 1, according to the Stern–Volmer<sup>30</sup> relation in eq 5 (derived from eqs 3 and 4). In eq 5,  $\phi_0$  is the quantum yield of pyridinium ylide

$$k_{\text{obs}} = k_0 + k_{\text{pyr}} [\text{pyridine}] + k_X [\text{heteroatom donor}] \quad (3)$$

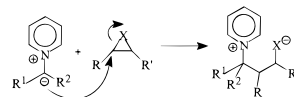
$$\phi = \frac{k_{\text{pyr}} [\text{pyridine}]}{k_{\text{pyr}} [\text{pyridine}] + k_X [\text{heteroatom donor}]} \quad (4)$$

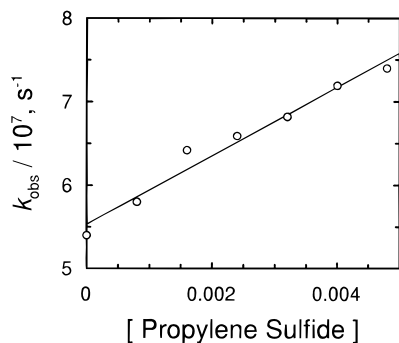
$$\frac{\phi_0}{\phi} = \frac{A^{\circ}_{\text{ylide}}}{A_{\text{ylide}}} = \frac{k_X}{k_{\text{pyr}} [\text{pyridine}]} [\text{heteroatom donor}] + 1 \quad (5)$$

formation in the absence of a second trap and  $\phi$  is the quantum yield of pyridinium ylide formation in the presence of trap.  $A^{\circ}_{\text{ylide}}$  is the intensity of the absorbance of pyridinium ylide **3a** in the absence of added trap, and  $A_{\text{ylide}}$  is the intensity of the absorbance of ylide **3a** in the presence of trap. A typical plot, for the reaction of **2a** with propylene sulfide, is shown in Figure 1 where the slope of the line is equal to  $k_X/k_{\text{pyr}}$  [pyridine]. The values for  $k_X$  were then calculated by using a known value<sup>4d</sup> for  $k_{\text{pyr}}$  of  $4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and known concentrations of pyridine.<sup>31</sup> Bimolecular rate constants of  $1.3 \times 10^7$ ,  $1.4 \times 10^8$ ,  $2.3 \times 10^9$ , and  $7.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , Table 1, were determined in this manner for the transfer of oxygen from propylene oxide, butadiene monoxide, pyridine *N*-oxide, and dimethyl sulfoxide (DMSO), respectively, to benzylchlorocarbene. The rate con-

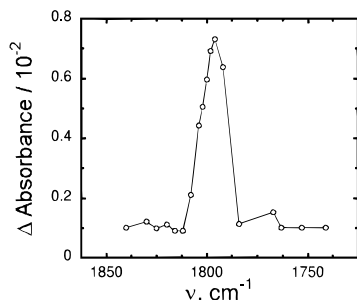
(30) Platz, M. S.; Modarelli, D. A.; Morgan, S.; White, W. R., III; Mullins, M.; Celebi, S.; Toscano, J. P. *Progress in Reaction Kinetics*; Rodgers, M. A., Ed.; Elsevier: Oxford, 1994; Vol. 19, p 93 and references therein.

(31) From Stern–Volmer quenching experiments it was found that the pyridinium ylide from carbene **2a** (and from the other carbenes and heteroatom donors studied here) reacted with the oxirane and thiirane traps with rate constants ranging from  $10^3$  to  $10^5 \text{ M}^{-1} \text{ s}^{-1}$ . For example, the pyridine ylide of benzylchlorocarbene reacts with butadiene monoxide with a rate constant of  $3.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . Probably the pyridinium ylides react with oxiranes and thiiranes via a nucleophilic ring opening reaction.





**Figure 2.** Plot of the pseudo-first-order rate constants for the decay of benzylchlorocarbene (monitored at 310 nm) vs [propylene sulfide] in cyclohexane at 22 °C.



**Figure 3.** Time resolved IR spectrum observed 500 ns after 308 nm LFP of **1a** in neat propylene oxide at 22 °C.

stants for transfer of oxygen from propylene oxide and from butadiene monoxide were measured in cyclohexane solvent, whereas those for transfer from pyridine *N*-oxide and from DMSO were measured in acetonitrile due to their insolubility in hydrocarbon media. A rate constant of  $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the transfer of a sulfur atom from propylene sulfide to benzylchlorocarbene was also measured in cyclohexane.

Alternatively,  $k_X$  can be obtained as the slope of the plot of observed rate constants of either the decay of carbene **2** using the kinetic expression in eq 6, or the growth of pyridine ylide (**3**),<sup>32</sup> versus heteroatom donor concentration using the kinetic expression in eq 3. Such a plot constructed from the pseudo-

$$k_{\text{obs}} = k_0 + k_X [\text{heteroatom donor}] \quad (6)$$

first-order rate constants for the decay of benzylchlorocarbene versus [propylene sulfide] in cyclohexane at 22 °C (Figure 2) yielded a value of  $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the reaction, which is in reasonable agreement with the value of  $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  determined by Stern–Volmer quenching of the yield of ylide **3a**. Here, the latter method is more reliable because of difficulties in determining accurate pseudo-first-order rate constants by measuring decays/growths, imposed by the time resolution of our instrument.<sup>33</sup>

**Laser Flash Photolysis: Infrared Detection.** The formation of phenylacetyl chloride was readily confirmed upon 308 nm LFP of **1** ( $1 \times 10^{-3} \text{ M}$ , continuous flow, purged with  $\text{N}_2$ ) in neat propylene oxide at 22 °C, by means of time-resolved infrared detection. An absorption assigned to phenylacetyl chloride, centered at  $1796 \text{ cm}^{-1}$ , was formed within the time resolution ( $\sim 500 \text{ ns}$ ) of our instrument (Figure 3).

(32) For examples of rates determined in these ways, see: refs 3, 4, 22, 23, and 24.

(33) For a description of laser flash photolysis with UV–vis detection, see: Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430.

**(b) Phenylchlorocarbene.** LFP (355 nm, 10 ns pulse, 40 mJ) of 3-chloro-3-phenyldiazirine (**1b**) in cyclohexane produced a long-lived transient (decays on the  $\mu\text{s}$  time scale) with  $\lambda_{\text{max}} \approx 315 \text{ nm}$  which has previously been assigned to phenylchlorocarbene (**2b**). LFP of **1b** in cyclohexane containing pyridine produced a transient signal associated with the pyridinium ylide of phenylchlorocarbene (**3b**) (stable on the ms time scale) with  $\lambda_{\text{max}} \approx 480 \text{ nm}$ . The rate constants for reaction of phenylchlorocarbene with heteroatom donors could be measured either by the decay of the carbene signal or by Stern–Volmer quenching of the pyridinium ylide signal as described above for benzylchlorocarbene. The latter was found to be most convenient due to the relative intensities of the two signals. The bimolecular rate constant for the reaction of carbene **2b** with propylene sulfide was measured in this manner and was found to be  $3.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  which is almost 2 orders of magnitude smaller than that of the analogous reaction with benzylchlorocarbene. The rate constant for the reaction of phenylchlorocarbene with propylene oxide could only be estimated on the basis of small changes in the decays of carbene signal and on small changes in pyridinium ylide amplitudes at high concentrations of trap.

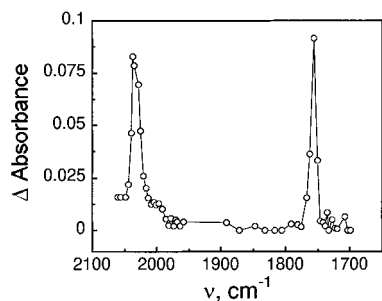
**(c) Methoxyphenylcarbene.** 3-Methoxy-3-phenyldiazirine (**1c**) was prepared by the exchange reaction of 3-bromo-3-phenyldiazirine with sodium methoxide in dimethylformamide (DMF) as described previously.<sup>9b,34</sup> Diazirine **1c** has a lifetime of 4–5 min at room temperature and does not survive for long periods even when stored on dry ice. Therefore, this precursor was prepared just prior to use. All solutions were prepared at  $-10$  to  $-30$  °C and warmed to room temperature just prior to photolysis. Fresh solutions were used for each kinetic measurement. We were able to reproduce the kinetic decays for methoxyphenylcarbene (**2c**) monitored at  $\lambda = 290 \text{ nm}$  and the slow growth for pyridinium ylide **3c** with  $k_{\text{pyr}} = 1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . The rate constant for the reaction between methoxyphenylcarbene (**2c**) and propylene sulfide was determined by monitoring the growth of pyridinium ylide at  $\lambda = 480 \text{ nm}$  and by monitoring the decay of the carbene signal at  $\lambda = 290 \text{ nm}$ . The kinetic runs were repeated several times and the rate constant for reaction was determined to be  $7.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . Attempts to measure the kinetics of oxygen atom transfer from propylene oxide to methoxyphenylcarbene (**2c**) were unsuccessful. The reaction was too slow even in neat propylene oxide.

**(d) Dialkylcarbenes.** Steady-state and laser flash photolysis experiments of oxadiazoline precursors have demonstrated the formation of diazoalkanes.<sup>25,26,35</sup> Figure 4 shows the time-resolved infrared spectrum following 308 nm LFP of precursor **6a**.

It has also been established that 308 nm LFP of oxadiazoline precursors, in the presence of pyridine, gives rise to pyridinium ylides and that these ylides arise from the trapping of the corresponding dialkylcarbenes.<sup>26</sup> Indirect evidence for the formation of dialkylcarbenes from oxadiazoline precursors was provided by comparison of pyridinium ylide spectra and lifetimes, obtained from an oxadiazoline precursor and from the corresponding diazirine precursor. These comparisons indicated that the pyridinium ylides from each precursor derive from capture of the same reactive intermediate (dimethylcarbene) by pyridine.<sup>26</sup>

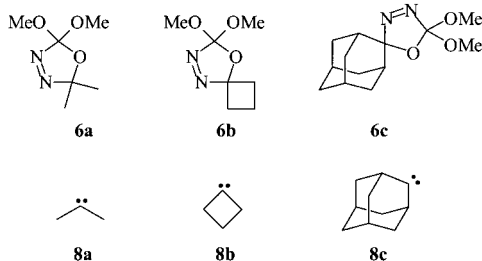
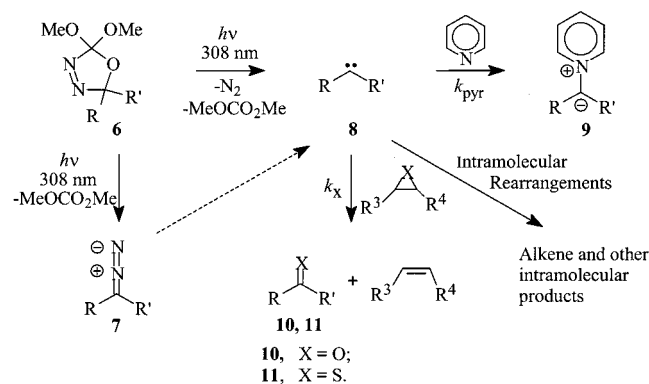
(34) Włostowski, M.; Moss, R. A.; Guo, W.; Chang, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 432.

(35) (a) Majchrzak, M. W.; Békhazi, M.; Tse-Sheepy, I.; Warkentin, J. *J. Org. Chem.* **1989**, *54*, 1842. (b) Majchrzak, M. W.; Jefferson, E. A.; Warkentin, J. *J. Am. Chem. Soc.* **1990**, *112*, 1842. (c) Jefferson, E. A.; Warkentin, J. *J. Org. Chem.* **1994**, *59*, 455. (d) Adam, W.; Finzel, R. *Tetrahedron Lett.* **1990**, *31*, 863.



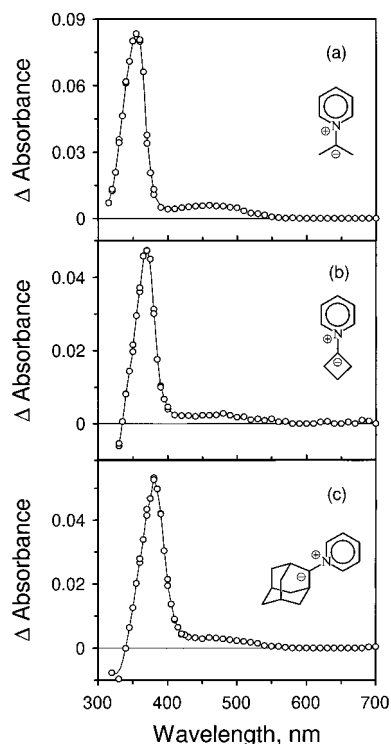
**Figure 4.** Time-resolved infrared spectrum recorded immediately following LFP of **6a** in cyclohexane at ambient temperature. The signal centered at  $2036\text{ cm}^{-1}$  is assigned to 2-diazopropane, and the signal at  $1756\text{ cm}^{-1}$  is assigned to dimethyl carbonate.

### Scheme 2

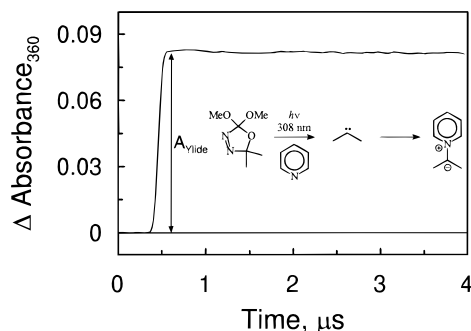


For precursors **6a–b** (Scheme 2), strong persistent bands with  $\lambda_{\text{max}}$  at approximately 360 nm were observed in the time-resolved UV–vis spectra and were assigned to the  $\pi\text{--}\pi^*$  transitions of the corresponding pyridinium ylide. Broad absorptions in the visible region of the spectra were assigned to the  $n\text{--}\pi^*$  transition of the corresponding pyridinium ylides (Figure 5a,b). A typical trace (Figure 6) shows that the growths of the pyridinium ylides were “instantaneous” (i.e., within the response time of the instrument).

Adamantylidene has been studied previously<sup>36,37</sup> and from 2-adamantane-2,3'-[3H]-diazirine a lifetime of  $\sim 2\ \mu\text{s}$ , dependent on diazirine precursor concentration, was determined. The pyridinium ylide of adamantylidene, absorbing at  $\sim 390\text{ nm}$  in benzene, was also reported.<sup>36a</sup> In the present study, the time-resolved UV–vis spectrum acquired (300–700 nm) after 308 nm LFP of oxadiazoline **6c** showed a strong persistent band with  $\lambda_{\text{max}} \approx 380\text{ nm}$ , assigned to the  $\pi\text{--}\pi^*$  transition of the pyridinium ylide of adamantylidene. A broad absorption in the visible region of the spectrum was assigned to the  $n\text{--}\pi^*$  transition of that ylide (Figure 5c). However, attempts to reproduce the reported slow kinetics for the reaction of



**Figure 5.** Time-resolved UV–vis spectrum observed following 308 nm LFP of **6a** in cyclohexane containing 0.5 M pyridine (a), of **6b** in cyclohexane containing 0.5 M pyridine (b), and of **6c** in cyclohexane containing 0.5 M pyridine at  $22\text{ }^\circ\text{C}$  (c). All spectra were collected 400 ns after the laser pulse.



**Figure 6.** The formation of pyridinium ylide of dimethylcarbene produced following UV-LFP of **6a** in cyclohexane containing 0.5 M pyridine at  $22\text{ }^\circ\text{C}$ .

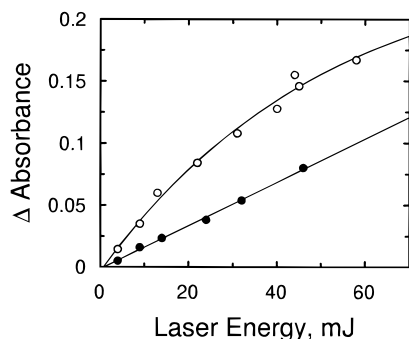
adamantylidene with pyridine by direct monitoring of the growth of the ylide absorption were unsuccessful. Rather, the ylide absorption was formed “instantaneously” (within the time resolution of our instrument) for the pyridine concentrations studied. Some of the earlier work is now known to be incorrect;<sup>38</sup> rate constants ( $k_{\text{pyr}}$ ) in cyclohexane and in benzene from both 2-adamantane-2,3'-[3H]-diazirine and oxadiazoline **6c**, have since been found to be  $2.6 \times 10^9$  and  $2.0 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ , respectively.<sup>38</sup>

Steady-state (SS) irradiation of 2,2-dimethoxy-5,5-dimethyl- $\Delta^3$ -1,3,4-oxadiazoline (**6a**) in cyclohexane- $d_{12}$  in a rayonet

(36) (a) Morgan, S.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2782. (b) Bally, T.; Matzinger, S.; Truttman, C.; Platz, M. S.; Morgan, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1964.

(37) Moss, R. A.; Chang, M. J. *Tetrahedron Lett.* **1981**, *22*, 3749.

(38) In a collaborative effort with Prof. Platz's group (Ohio State) we have investigated the photochemistry of this precursor and the corresponding diazirine precursor. New results regarding adamantylidene, including updated lifetimes and rate constants for its reaction with pyridine have been accepted for publication: Pezacki, J. P.; Warkentin, J.; Wood, P. D.; Luszyk, J.; Yuzawa, T.; Gudmundsdottir, A. D.; Morgan, S.; Platz, M. S. *J. Photochem. Photobiol. A Chem.* Other groups have come to similar conclusions regarding adamantylidene. See: Bonneau, R.; Liu, M. T. H.; Hellrung, B.; Wirz, J. *J. Photochem. Photobiol. A Chem.* Accepted for publication.



**Figure 7.** Laser energy vs the change in maximum absorbance plot, measured after 308 nm laser flash photolysis of **6a** in cyclohexane and in cyclohexane containing 0.5 M pyridine, for 2-diazopropane at 250 nm (○) and for the pyridinium ylide of dimethylcarbene at 360 nm (●).

reactor fitted with 300 nm bulbs gave, even after prolonged exposure (12 h, ambient temperatures), only trace amounts of propene (1–2%) from facile 1,2-H migration in dimethylcarbene (sealed NMR tube experiments). Similar low yields of cyclobutene and methylenecyclopropane (carbene rearrangement products) were observed from 300 nm SS photolysis of precursor **6b** in cyclohexane-*d*<sub>12</sub>. Precursor **6c** gave dehydroadamantane and adamantanone azine in 1–5% yields in cyclohexane-*d*<sub>12</sub>. The major products were the corresponding diazoalkanes which could be monitored spectroscopically by <sup>1</sup>H NMR or by UV. The diazoalkanes slowly formed azine products with very little (<5%) carbene rearrangement products being formed upon standing at room temperature even at concentrations of 10<sup>-3</sup> M. This suggests that a mechanism other than the reaction of carbenes **8a–c** with their corresponding diazoalkanes **7a–c** is responsible for the formation of azine products.<sup>39</sup> In contrast to the very low yields of carbene derived products in SS experiments (300 nm), 308 nm LFP converts oxadiazolines to carbenes efficiently enough for kinetic analysis to be performed. In SS experiments, 300 and 250 nm light are required simultaneously in order to produce carbenes efficiently at room temperature. The LFP method could involve multiphoton processes which are not likely to occur in SS photolysis. To test whether carbene formation in the 308 nm LFP of **6a–c** occurs via a multiphoton process, solutions of precursor **6a** in cyclohexane and in cyclohexane containing 0.5 M pyridine were irradiated (308 nm LFP) over a range of laser energies. Changes in the intensities of absorbance were monitored at λ = 250 nm for 2-diazopropane and at λ = 360 nm for the pyridine ylide of dimethylcarbene. Surprisingly, our data, Figure 7, seem to indicate that both 2-diazopropane and dimethylcarbene are formed in monophoton processes, with the former showing saturation.

The ratios  $k_X/k_{\text{pyr}}$  [pyridine] for the reactions of dimethylcarbene (**8a**), cyclobutylidene (**8b**), and adamantylidene (**8c**) with heteroatom donors were determined by 308 nm LFP of the corresponding oxadiazoline precursors **6a–c** by means of the pyridine ylide method, using the Stern–Volmer treatment in the same manner as described for carbene **2a** (eq 5). However, the values for  $k_{\text{pyr}}$  were not measurable for carbenes **8a,b** because signals for pyridinium ylides **9a,b** were not

(39) If dimethylcarbene has a lifetime of ~20 ns in hydrocarbon solvent at room temperature then the rate constant for 1,2-H migration (unimolecular disappearance of the carbene) is  $k_{1,2\text{H}} = 5 \times 10^7 \text{ s}^{-1}$ . Assuming that dimethylcarbene traps 2-diazopropane with a rate constant of  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  then, at concentrations of 10<sup>-3</sup> M diazoalkane, the product ratio should be ~10:1 in favor of intramolecular rearrangement and not the observed >9:1 ratio of acetone azine to propene (<sup>1</sup>H NMR, sealed tube).

**Table 1.** Rate Constants for Quenching of Carbenes with Oxygen and Sulfur Atom Donors at 22 °C

Carbene	Heteroatom Donor	$k_X / k_{\text{vide}}$	$k_X, \text{M}^{-1} \text{s}^{-1}$
	Propylene Oxide	$1.6 \times 10^2$	$(1.6 - 8.0) \times 10^{7\text{a,b}}$
	Cyclohexene Oxide	$1.5 \times 10^2$	$(1.5 - 7.5) \times 10^{7\text{a,b}}$
	Butadiene Monoxide	$7.6 \times 10^2$	$(0.76 - 3.8) \times 10^{8\text{a,b}}$
	Propylene Sulfide	3.3	$(0.33 - 1.65) \times 10^{10\text{a,b}}$
	Propylene Oxide	$3.9 \times 10^2$	$(0.39 - 2.0) \times 10^{8\text{a,b}}$
	Butadiene Monoxide	$6.3 \times 10^2$	$(0.63 - 3.2) \times 10^{8\text{a,b}}$
	Propylene Sulfide	7.7	$(0.77 - 3.9) \times 10^{10\text{a,b}}$
	Propylene Oxide	$1.9 \times 10^2$	$4.9 \times 10^{7\text{b,c}}$
	Butadiene Monoxide	$5.3 \times 10^2$	$1.4 \times 10^{8\text{b,c}}$
	Propylene Sulfide	5.6	$1.5 \times 10^{10\text{b,c}}$
	Propylene Oxide	$3.2 \times 10^3$	$1.3 \times 10^{7\text{b,d}}$
	Butadiene Monoxide	$3.3 \times 10^2$	$1.4 \times 10^{8\text{b,d}}$
	Propylene Sulfide	$6.0 \times 10^1$	$2.5 \times 10^{9\text{b,d}}$
	DMSO	$5.5 \times 10^1$	$2.3 \times 10^{9\text{d,f}}$
	Pyridine N-Oxide	1.7	$7.1 \times 10^{9\text{d,f}}$
	Propylene Sulfide	$1.5 \times 10^2$	$3.2 \times 10^{8\text{e,g}}$
	<i>cis</i> -2-butene oxide	$4.4 \times 10^2$	$9.2 \times 10^{8\text{e,h}}$
	<i>trans</i> -2-butene oxide	$1.5 \times 10^2$	$3.2 \times 10^{8\text{e,h}}$
	Propylene Sulfide	$4.8 \times 10^2$	$3.6 \times 10^{7\text{b,i}}$
	Propylene Oxide	$\sim 5 \times 10^4$	$\sim 4 \times 10^{5\text{b,i}}$
	Propylene Sulfide	$5.9 \times 10^1$	$7.1 \times 10^{4\text{d,j}}$
	Propylene Oxide	k	k

<sup>a</sup> Assuming  $k_{\text{pyr}} = (1-5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>b</sup> In cyclohexane. <sup>c</sup>  $k_{\text{pyr}} = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>38</sup> see text. <sup>d</sup>  $k_{\text{pyr}} = 4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>41</sup> see text. <sup>e</sup> Measured from the decays of the carbene, monitored at 310 nm. <sup>f</sup> In acetonitrile. <sup>g</sup> Measured using the changes in maximum absorbance of the MeCN ylide monitored at 400 nm as a function of propylene sulfide and assuming a rate constant of  $k_{\text{MeCN}} = 2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>h</sup> Taken from ref 17a, assuming  $k_{\text{MeCN}} = 2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , see text. <sup>i</sup>  $k_{\text{pyr}} = 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>8</sup> <sup>j</sup>  $k_{\text{pyr}} = 1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>9b</sup> <sup>k</sup> Too small to measure.

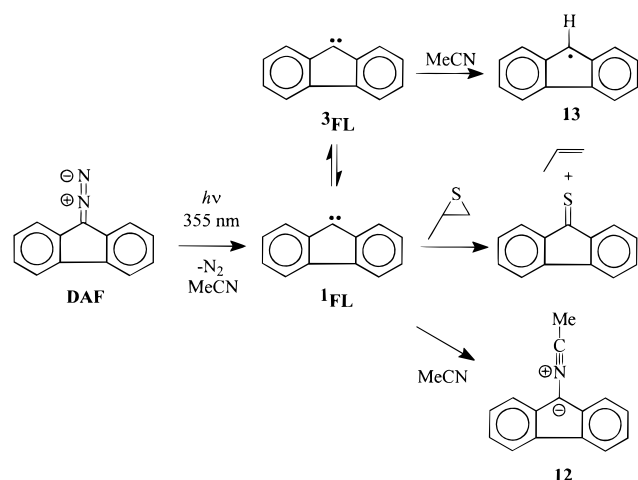
detectable at concentrations of pyridine necessary to observe growths with our instrument (i.e., the unimolecular rearrangements are the dominant reaction pathway of these carbenes at lower concentrations of pyridine). Therefore, we have made the assumption that the values of  $k_{\text{pyr}}$  for these carbenes should fall between 1 and  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  based on literature data for carbenes of similar structure.<sup>3,5</sup> Given that adamantylidene reacts with pyridine with rate constants similar to those of other dialkylcarbenes,<sup>3-5</sup> its reactivity in heteroatom transfer reactions then closely resembles those of the other dialkylcarbenes studied here. The ranges of rate constants for these reactions are summarized in Table 1.

**Laser Flash Photolysis: Infrared Detection.** A TRIR-LFP study of **6a** in cyclohexane (308 nm,  $2.3 \times 10^{-2} \text{ M}$ , continuous flow, purged with N<sub>2</sub>) led to absorption bands at  $2036 \pm 3 \text{ cm}^{-1}$ , assigned to the diazo band of 2-diazopropane, and at  $1756 \pm 3 \text{ cm}^{-1}$ , assigned to the carbonyl band of dimethyl carbonate (Figure 4). There were no other absorption bands in the 2160–1690  $\text{cm}^{-1}$  region of the IR. Formation of acetone upon 308 nm LFP of **6a** in 5.0 M cyclohexene oxide in pentane at 22 °C was readily confirmed by means of TRIR detection.<sup>40</sup> Absorptions assigned to the carbonyl band of dimethyl carbonate (Figure 4), centered at  $1756 \text{ cm}^{-1}$ , and to acetone, centered at  $1724 \text{ cm}^{-1}$ , were formed instantaneously (i.e., within the response time of the instrument) after 308 nm TRIR-LFP.

**(e) Fluorenylidene.** Rate constants for the oxygen atom transfer reactions from epoxides to spin-equilibrated fluore-

(40) A laser flash photolysis system with a Mutek MPS-1000 diode laser (output 1520–2314  $\text{cm}^{-1}$ ) as the monitoring source was used. Wagner, B. D.; Arnold, B. R.; Brown, G. S.; Luszyk, J. *J. Am. Chem. Soc.* **1998**, *120*, 1827.

## Scheme 3

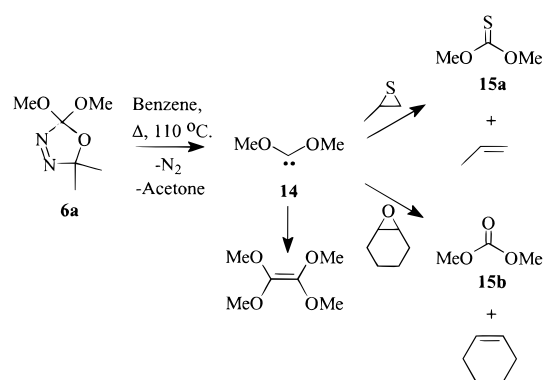


nylidene (**FL**) have been measured previously by Stern–Volmer quenching of the acetonitrile ylide of **FL** in acetonitrile solutions.<sup>17a</sup> Upon 355 or 337 nm LFP of **DAF** in N<sub>2</sub>-saturated acetonitrile three transients are observable centered at 400, 470, and 500 nm.<sup>41</sup> These signals are associated with ylide **12**, triplet fluorenylidene (**<sup>3</sup>FL**), and fluorenyl radical **13** (Scheme 3).

The half-life of spin-equilibrated fluorenylidene in acetonitrile solution is ~17 ns which corresponds to a rate constant of  $2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>17a</sup> which is assumed here to be the rate constant for the formation of ylide **12**. Using Stern–Volmer methods analogous to those used for pyridine quenching above, we have measured the rate constant for the sulfur atom transfer reaction from propylene sulfide to spin equilibrated fluorenylidene, using fresh solutions of **DAF** for each concentration of sulfide. No signals which could be attributed to either a propylene sulfide ylide of fluorenylidene, or to radical intermediates other than **13**, were detected in time-resolved UV–vis spectra recorded for a range of trap concentrations. The rate constant for sulfur atom transfer was determined to be  $3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . This reaction could not be followed in cyclohexane because of the rapid formation of the fluorenyl radical **13** by hydrogen atom abstraction from the solvent.

**Steady-State Photolysis.** Analyses of oxygen and sulfur atom transfer reactions were also carried out using steady-state photolytic methods. Dialkylcarbenes **7a–c** were generated using dual wavelength irradiations with both 250 and 300 nm light, as described previously.<sup>26</sup> Adamantylidene and cyclobutylidene were generated in this manner in both neat propylene oxide and in 0.1 M propylene sulfide in hexadecane. The reaction mixtures were analyzed by GC-MS, and it was found that the corresponding oxygen and sulfur atom transfer products were formed. In all reactions higher molecular weight products were also observed, but they are attributed to products of direct irradiation of propylene oxide, and propylene sulfide, in the steady-state experiments. Dimethylcarbene was also generated in this manner in both neat propylene oxide and in 0.1 M propylene sulfide in hexadecane, but the analysis of the products was not achieved due to the similarity between the products

## Scheme 4



and reactants. Carbenes **7a–c** were also generated (250 and 300 nm, SS) in the presence of neat butadiene monoxide. In most cases, the corresponding oxygen atom transfer products were observed by GC-MS. Mass spectra attributed to cyclopropanation of butadiene monoxide were also observed. In most cases it was not possible to determine the ratios of these competing pathways due to secondary photolysis products. An exception was the reaction of adamantylidene with butadiene monoxide for which a ratio of ~3:1 for oxygen transfer versus cyclopropanation was observed. The reactions of benzylchlorocarbene, generated by photolysis of diazine **1a** (350 nm, SS), with propylene oxide, propylene sulfide, and butadiene monoxide were also investigated. Yields of oxygen and sulfur atom transfer products were difficult to obtain due to HCl production in the photochemical reaction.<sup>19</sup> Phenyl thioacetyl chloride was detected by GC-MS (MS, *m/z* 170 (<sup>35</sup>Cl), 172 (<sup>37</sup>Cl)) for the reaction of carbene **2a** with propylene sulfide (0.1 M in hexadecane).

**Thermal Generation of Dimethoxycarbene.** Thermolyses of oxadiazoline **5a** (0.1 M) in the presence of either cyclohexene oxide or propylene sulfide (0.1 M) were performed in benzene in sealed tubes (degassed) for 24 h at 110 °C. The resulting mixtures were analyzed by <sup>1</sup>H NMR (500 MHz) and GC-MS. Products associated with oxygen and sulfur transfer were detected in both cases. The major product was found to be tetramethoxyethylene, the dimerization product of dimethoxycarbene (Scheme 4). For the reaction of dimethoxycarbene with cyclohexene oxide, cyclohexene and dimethyl carbonate (**15b**) were detected in ~0.9% yields relative to internal standard *p*-xylene. Their GC-MS spectra were compared with those of authentic commercial samples. Neither of these products was detected in control experiments that involved heating of cyclohexene oxide in the absence of **5a**, or the thermolysis of **5a** alone. Thermal decomposition of **5a** in the presence of propylene sulfide led to the formation of propylene and dimethyl thiocarbonate (**15a**) in ~15% yield; the major product again being tetramethoxyethylene. In both reactions unobscured alkene proton signals in the <sup>1</sup>H NMR spectra were attributed to cyclohexene and propene, respectively.

## Discussion

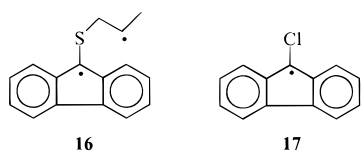
**Possible Mechanisms for Heteroatom Transfer.** Bimolecular rate constants for oxygen transfer to carbenes **8a–c** were of the order of 10<sup>7</sup> to 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> and those for sulfur atom transfer were of the order of 10<sup>9</sup> to 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>. These reactions are presumably those of the singlet carbenes. Dimethylcarbene is now believed to have a singlet ground state, with ΔE<sub>ST</sub> calculated to be ~1.6 kcal mol<sup>-1</sup>,<sup>42–44</sup> and intersystem

(41) (a) Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 5958. (b) Senthilnathan, V. P.; Platz, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7637. (c) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 5934. (d) Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 944. (e) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6813. (f) Griller, D.; Hadel, L. M.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227. (g) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Am. Chem. Soc.* **1985**, *107*, 7204. (h) Barcus, R. L.; Wright, B. B.; Leyva, E.; Platz, M. S. *J. Phys. Chem.* **1987**, *91*, 6677.

(42) Matzinger, S.; Fülischer, M. P. *J. Phys. Chem.* **1995**, *99*, 10747.

crossing (ISC) is competitive with 1,2-hydrogen migration.<sup>4d-f</sup> When ISC is rapid compared to product forming steps, then the product ratio is determined entirely by the relative transition-state energies for formation of products and the singlet/triplet populations are irrelevant, according to the Curtin–Hammett principle.<sup>45</sup> Triplet reactions generally have higher barriers than singlet reactions unless the reactant (e.g., O<sub>2</sub>) is prone to radical chemistry. Oxiranes are not good substrates for reactions with carbon-centered radicals. As far as we know there is no precedence for hydrogen atom abstraction from a ring carbon of a cyclopropyl system by a carbon centered radical. Oxiranymethyl radicals<sup>46</sup> open rapidly to allyloxy radicals (in general) but show either C–C or C–O bond scission depending on substituent.<sup>47</sup> For the case of the reaction of a triplet carbene with epoxides, oxiranymethyl radicals would have to be formed first by H-abstraction, from the methyl group of propene oxide for example. Carbon-centered radicals, which are good models for triplet carbenes, are poor abstractors of hydrogen from saturated carbon atoms, especially primary hydrogens. Similar arguments apply to thiiranes except for the added possibility of radical attack (S<sub>H</sub>2) at sulfur. Tributyltin radicals have recently been shown to abstract sulfur atoms from thiiranes to yield alkene products in high yields.<sup>48</sup>

Cyclobutylidene chemistry is dominated by singlet-state behavior as evidenced by a lack of a significant solvent deuterium isotope effect on its lifetime in solution.<sup>26</sup> Although it is possible that dimethylcarbene (**8a**), adamantylidene (**8c**), or fluorenylidene (**Fl**) react with oxiranes and thiiranes by hydrogen atom abstraction or S<sub>H</sub>2 substitution at oxygen or sulfur, because all of these carbenes have low-lying and accessible triplet states, it is likely that singlet state chemistry is dominant because of the high reactivity of singlets toward heteroatom lone pairs.<sup>3,4</sup> If triplet fluorenylidene (<sup>3</sup>Fl) reacted with propylene sulfide by an S<sub>H</sub>2 substitution mechanism at sulfur we would expect the formation of diradical **16** by LFP. The 9-chloro-9-fluorenyl radical (**17**, ~480 nm) is easily detectable by LFP when <sup>3</sup>Fl abstracts a chlorine radical from carbon tetrachloride.<sup>41f</sup> Our failure to observe **16** may reflect its short lifetime.



Fluorenylidene also reacts with sulfides and disulfides with rate constants ranging between 10<sup>8</sup> and 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> to produce transient sulfur ylides with λ<sub>max</sub> between 350 and 450 nm.<sup>49</sup>

(43) Richards, C. A., Jr.; Kim, S.-J.; Yamaguchi, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1995**, *117*, 10104.

(44) Sulzbach, H. M.; Bolton, E.; Lenoir, D.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1996**, *118*, 9908.

(45) (a) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111. (b) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

(46) Gash, R. C.; MacCorquodale, F.; Walton, J. C. *Tetrahedron* **1989**, *45*, 5531.

(47) (a) Ziegler, F. E.; Petersen, A. K. *J. Org. Chem.* **1995**, *60*, 2666.

(b) Ziegler, F. E.; Petersen, A. K. *J. Org. Chem.* **1994**, *59*, 2707. (c) Dickinson, J. M.; Murphy, J. A.; Patterson, C. W.; Wooster, N. F. *J. Chem. Soc., Perkin Trans 1* **1990**, 1179. (d) Stogryn, E. L.; Gianni, M. H. *Tetrahedron Lett.* **1970**, 3025.

(48) Izraelwicz, M. H.; Nur, M.; Spring, R. T.; Turos, E. *J. Org. Chem.* **1995**, *60*, 470.

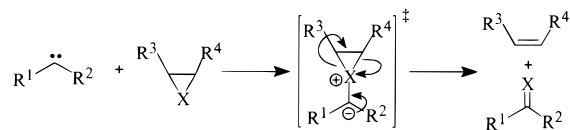
(49) (a) Alberti, A.; Griller, D.; Nazran, A. S.; Pedulli, G. F. *J. Am. Chem. Soc.* **1986**, *108*, 3024. (b) McGimpsey, W. G.; Scaiano, J. C. *Tetrahedron Lett.* **1986**, *27*, 547.

The lack of any detectable intermediates in the reaction between Fl and propylene sulfide therefore implies a concerted mechanism.

The fact that bimolecular rate constants obtained for benzylchlorocarbene (**2a**), a known ground-state singlet, with oxygen and sulfur atom donors were similar to those for **8a–c** is consistent with the interpretation that all of the abstractions are predominantly or exclusively singlet-state reactions. Thus, while the observed rate constants for oxygen and sulfur atom transfers represent the sum of all reactions of a carbene with a trap, it is reasonable to assume that they adequately represent the absolute rate constants for singlet processes. Phenylchlorocarbene (**2b**) and methoxyphenylcarbene (**2c**) are also ground-state singlet carbenes and differences in their absolute reactivities are most likely due to substituent effects on the carbene carbon rather than differences in intersystem crossing (ISC) rate constants leading to triplet-state chemistry. An example of the differences in reactivities of singlet phenylchlorocarbene (**2b**) and methoxyphenylcarbene (**2c**) is their propensity to undergo electrophilic attack onto the lone pair on the nitrogen atom in pyridine to form pyridinium ylides ( $k_{\text{pyr}} = 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for **2b** and  $k_{\text{pyr}} = 1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for **2c** in hydrocarbon solvent at ambient temperatures).<sup>9b,10</sup>

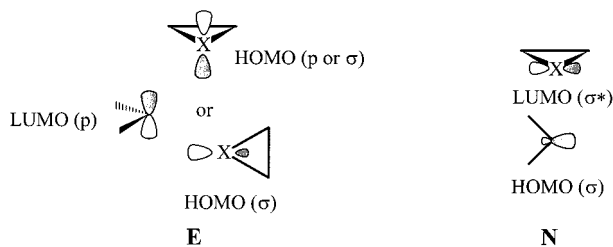
Oxonium ion intermediates have been implicated during oxygen atom transfer from oxiranes to fluorenylidene, although such intermediates were not detectable via UV-LFP experiments.<sup>17a</sup> Intermediates were not observed for any of the reactions of epoxides and sulfides with carbenes **2a–c**, **8a–c**, and **Fl**, by UV-LFP. Here, acetone and phenylacetyl chloride were formed “instantaneously” from reactions of dimethylcarbene with cyclohexene oxide and of benzylchlorocarbene with propylene oxide, as observed by 308 nm laser flash photolysis with time-resolved infrared detection (TRIR-LFP). An upper limit for the lifetimes of the cyclohexene oxide ylide of dimethylcarbene and the propylene oxide ylide of benzylchlorocarbene can therefore be placed at ~500 ns, which corresponds to the rise time of the TRIR system.

The atom transfer reactions to electrophilic carbenes are fast reactions, which implies that they are exothermic. The thermodynamic driving force can be understood from the fact that while two σ bonds are being broken, they are strained σ bonds which are replaced by one σ and two π bonds. One π bond is that of the strong carbonyl double bond. Although the LFP results did not confirm or exclude the formation of oxonium ion or sulfonium ion intermediates, other sulfur ylides from the reactions of sulfides and disulfides with **Fl** have been observed directly by LFP,<sup>49</sup> suggesting that the barriers, if any, from ylide intermediates to products are small. It is possible that heteroatom transfer from oxiranes and thiiranes might occur via ylide-like transition states rather than through a persistent ylide intermediate which then fragments.



Reactions of ambiphilic and electrophilic carbenes **2a** and **8a–c** with butadiene monoxide may follow oxygen transfer and cyclopropanation pathways, as evidenced by product studies. Therefore, for the reactions of carbenes **2a** and **8a–c** with butadiene monoxide, the observed quenching rate constants represent the sum of both processes. Since oxygen transfer is favored (~3:1) over cyclopropanation, the majority of the





**Figure 8.** HOMO–LUMO interactions in oxygen and sulfur abstraction reactions between carbenes and oxiranes and thiiranes.

quenching of these carbenes must occur via the oxygen atom transfer manifold. It is possible therefore that oxygen transfer rates are accelerated relative to those from propylene oxide as a result of increased stabilization of the transition state by the alkene substituent, and also by the additional thermodynamic stability of the butadiene product.

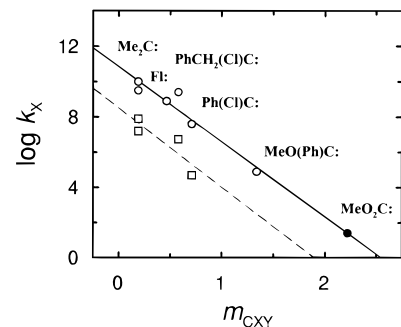
**Frontier Molecular Orbital Theory.** Carbene selectivities have been successfully predicted using frontier molecular orbital theory.<sup>6a,b,50</sup> Differential orbital energies ( $\Delta\epsilon_E$  and  $\Delta\epsilon_N$ ) for oxygen, sulfur, and nitrogen atom transfer reactions from ethylene oxide, ethylene sulfide, and aziridine to phenylchlorocarbene (**2b**), methoxyphenylcarbene (**2c**), dimethylcarbene (**8a**), cyclobutylidene (**8b**), fluorenylidene (**FL**), and dimethoxycarbene (**14**) were calculated at the RHF/6-31+G\*\*//RHF/6-31+G\* and the MP2/6-311+G\*\*//MP2/6-311+G\* using Gaussian 94 (Supporting Information).<sup>51</sup> The nucleophilic orbital interactions,  $\Delta\epsilon_N$ , (N, carbene  $\sigma$  with donor  $\sigma^*$  orbital) were calculated to be either dominant for the case of reactions with ethylene oxide, or else equal to the electrophilic interactions,  $\Delta\epsilon_E$ , as is the case for ethylene sulfide and aziridine (**E**, carbene p orbital with heteroatom donor  $\sigma$  orbital), Figure 8. Given the charge distribution in the ylide transition states, it is surprising that the nucleophilic orbital interactions (**N**) dominate for reactions with ethylene oxide. For a given carbene, the differential orbital energies are lower for sulfur than for oxygen or nitrogen which is consistent with an increase in nucleophilic character for the sulfur-containing heteroatom donors. However, the magnitudes of the differential orbital energies do not reflect the observed rate constants for the carbenes, especially on going from highly electrophilic to more nucleophilic carbenes. If one considers only carbene (LUMO)–heteroatom donor (HOMO) interactions ( $\Delta\epsilon_E$ , i.e., electrophilic attack), then FMO theory would predict negligible reactivity differences between electrophilic and more nucleophilic carbenes. It is possible that smaller orbital coefficients (carbene LUMO) and favorable electrostatic interactions are responsible for the high rate constants for heteroatom transfer to electrophilic dialkylcarbenes as compared with those to nucleophilic carbenes.<sup>52</sup>

**Carbene Philicity and Heteroatom Transfer.** The reactivities of carbene intermediates may be predicted based on

(50) (a) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley-Interscience: New York, 1976. Also see refs 6 and 28.

(51) (a) Gaussian 94, Revision D.4; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995. (b) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (c) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244. (d) Hehre, W. J.; Radom, L.; Pople, J. A.; Schleyer, P. v. R. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986. (e) NBO Version 3.1; Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.

(52) See ref 5 for similar arguments.



**Figure 9.** Plots of  $\log k_X$  vs  $m_{CXY}$  for the abstraction of oxygen atoms from propylene oxide (open squares) and for sulfur atoms from propylene sulfide (open circles). The closed circle is an extrapolated point for the reaction of dimethoxycarbene with propylene sulfide.

Moss' carbene philicity scale  $m_{CXY}$ .<sup>6a,b,28,53</sup> Values for  $m_{CXY}$  can be determined empirically on the basis of selectivities of carbenes toward olefins or they can be predicted using  $\sigma_R^+$  and  $\sigma_I$  which relate the degree of resonance interactions and the inductive effects between a substituent and the carbene carbon to the carbene's reactivity. The expression which relates  $\sigma_R^+$  and  $\sigma_I$  to  $m_{CXY}$  is in eq 7.

$$m_{CXY} = -1.10 \sum_{X,Y} \sigma_R^+ + 0.53 \sum_{X,Y} \sigma_I - 0.31 \quad (7)$$

Values for  $m_{CXY}$  were calculated for carbenes **2a–c**, **8a–c**, and **14** using eq 7.<sup>6a,b,54</sup> Least-squares fitting of  $\log k_X$  versus  $m_{CXY}^{\text{calcd}}$  to the equation for a straight line, for the rate constants for sulfur atom transfer from propylene sulfide to the carbenes studied, gave a slope of  $-4.2$ , with a correlation coefficient of  $R = 0.96$ . A similar slope was found for the least-squares fitting of  $\log k_X$  versus  $m_{CXY}^{\text{calcd}}$  for the rate constants for oxygen atom transfer from propylene oxide, Figure 9.

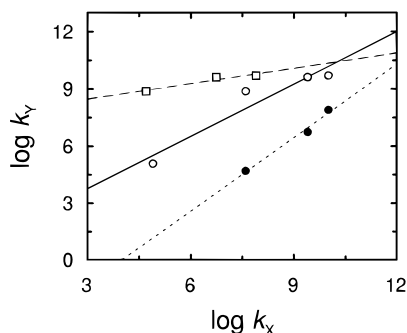
The linear free energy relationship between the barriers for heteroatom transfer and calculated  $m_{CXY}$  values indicates that the reaction is sensitive to carbene philicity and that electrophilic carbenes will undergo heteroatom transfer more readily than their nucleophilic counterparts.<sup>55,56</sup> For the reaction of dimethoxycarbene (**14**) with oxiranes and thiiranes, high yields of carbene dimer imply that the rate constants for oxygen and sulfur atom transfer are several orders of magnitude lower than those for more electrophilic carbenes. Carbene **14**, considered to be an "archetypal" nucleophilic carbene, has a lifetime of  $\sim 2$  ms in dilute solution at ambient temperatures with dimerization being the main pathway by which it is consumed.<sup>30</sup> That lifetime

(53) (a) Moss, R. A.; Young, C. M.; Perez, L. A.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1981**, *103*, 2413. (b) Moss, R. A.; Mallon, C. B.; Ho, C.-T. *J. Am. Chem. Soc.* **1977**, *99*, 4105.

(54) Values of  $\sigma_R^+$  and  $\sigma_I$  from (a) O. Exner In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds; Plenum Press: New York, 1978. (b) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119.

(55) We have attempted to generate a similar linear free energy relationship for the reactions of various carbenes with pyridine. From the data in ref 5 as well as other data from the literature, we do find a linear free energy relationship with a leveling effect (rate constants at least partially diffusion controlled) for more electrophilic carbenes where factors other than philicity govern small changes in rate constants for reaction (e.g., pyridinium ylide stabilities and changes in heavy atom bond angles and distances). However, some carbenes, most notably phenylfluorocarbene, do not follow the trend for unknown reasons. It may be fortuitous that we chose "well-behaved" carbenes here. There is no question that rate constants for the reactions of carbenes with pyridine do decrease for carbenes with increasing nucleophilic character, at least qualitatively. A recent discovery regarding the formation of  $\pi$ -complexes from carbenes and arenes, which should also be possible for pyridine, may complicate the picture mechanistically.<sup>56</sup>

(56) Moss, R. A.; Yan, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1998**, *120*, 1088.



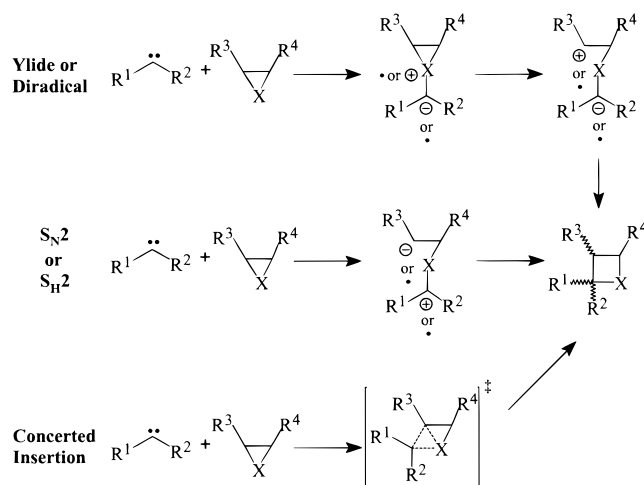
**Figure 10.** Plots of  $\log k_X$  vs  $\log k_Y$ . The open circles are  $\log k_X$  (propylene sulfide) vs  $\log k_{\text{pyr}}$  data and the solid line represents the linear least-squares fit. Open squares are  $\log k_X$  (propylene oxide) vs  $\log k_{\text{pyr}}$  data, and the dashed line is the linear least-squares fit. The filled circles are  $\log k_X$  (propylene sulfide) vs  $\log k_X$  (propylene oxide) data, and the dotted line is the linear least-squares fit.

must depend on carbene concentration (the reaction is bimolecular) and is expected to be shorter at 110 than at 22 °C. Nevertheless, a strong preference for this carbene to undergo dimerization over heteroatom transfer is in keeping with small rate constants for reaction of carbenes of similar structure with pyridine. Extrapolation of the line in Figure 10 gives a predicted rate constant for the reaction of dimethoxycarbene with propylene sulfide of  $\sim 2.6 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$ , a value too small to be confirmed by LFP techniques but large enough to lead to heteroatom transfer if the steady-state concentration of carbene is low enough.

Linear least-squares fitting of  $\log k_X$  versus  $\log k_{\text{pyr}}$  for sulfur atom transfer from propylene sulfide gave a straight line with slope 0.9 for sulfur atom transfer from propylene sulfide and a slope of 0.2 for oxygen atom transfer from propylene oxide. These correlations are consistent with the mechanistic interpretation that heteroatom transfer occurs from the singlet states of carbenes and by electrophilic attack of the carbene carbon onto the heteroatom lone pair of the donor toward either an ylide intermediate or a transition state that is ylide-like. Linear least-squares fitting of  $\log k_X$  for the reactions with propylene sulfide versus  $\log k_X$  for the reactions with propylene oxide gave a straight line with a slope of 1.3 with a correlation coefficient of  $R = 0.99$  suggesting that both heteroatoms are abstracted by the same mechanism.

While oxetanes were not observed in the oxygen transfer reactions studied here, they have been reported previously.<sup>17c</sup> For the reaction of carboethoxycarbene with styrene oxide, anionic charge buildup at the carbene carbon as the ylide species is being formed is highly stabilized by the carboethoxy substituent, whereas positive charge buildup at oxygen and at one of the epoxide carbons is also stabilized by the phenyl group. Oxetane formation can occur by either a stepwise mechanism involving the formation of an oxonium ylide which then opens to give a charge separated species (Scheme 5, upper pathway), a concerted mechanism involving selective cleavage of only one epoxide C–O bond to form a charge separated intermediate (Scheme 5, middle pathway), or a fully concerted insertion of the carbene into the C–O bond of the epoxide (Scheme 5, lower pathway). Given that insertion products were not observed in the reactions studied here, it is unlikely that a fully concerted mechanism is responsible for oxetane formation in the case of the reaction of carboethoxycarbene with styrene oxide. The intermediacy of a charge separated zwitterionic intermediate via a selective ring opening seems more likely and further investigations of the crossover from heteroatom transfer to oxetane formation are pending.

### Scheme 5



### Conclusions

Absolute rate constants for heteroatom transfer from propylene oxide and propylene sulfide to carbenes **2a–c** and **6a–c** measured here range from  $10^4$  to  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  at 22 °C and appear to obey linear free energy relationships with respect to the carbene philicity parameter  $m_{\text{CXY}}$ . Electrophilic carbenes, such as singlet dimethylcarbene (**6a**), cyclobutylidene (**6b**), and adamantylidene (**6c**) are more reactive toward heteroatom donors whereas ambiphilic carbenes, exemplified by phenylchlorocarbene (**2b**) and methoxyphenylcarbene (**2c**), are less reactive. Dimethoxycarbene, considered to be nucleophilic in character, is much less reactive toward propylene sulfide and cyclohexene oxide than the electrophilic/ambiphilic carbenes above. Although absolute rate constants are not known, the fact that tetramethoxyethylene was the major product in each case (at 110 °C,  $[\text{trap}] = 0.1 \text{ M}$ ) strongly suggests that encounters between dimethoxycarbene and those substrates do not generally result in reaction. Ylides from the reaction of carbenes with oxiranes and thiranes were not observed by LFP methods. Benzylchlorocarbene also abstracts the oxygen atom from DMSO and from pyridine-*N*-oxide with rate constants exceeding  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  at 22 °C.

### Experimental Section

**General Information.** NMR spectra were determined with either Bruker DRX 500 or Bruker AC 200 spectrometers. Chemical shifts are reported in parts per million relative to TMS as internal standard. GC-MS analyses were carried out with a Hewlett-Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-1 capillary column (12m  $\times$  0.2 mm; Chromatographic Specialties, Inc.). UV-vis spectra were measured on a Varian Cary 3 double-beam spectrophotometer. Mass spectra were obtained on a VG Analytical ZAB-E double-focusing mass spectrometer. Infrared spectra were obtained with a Bio-Rad FTS-40 spectrometer from samples in KBr windows.

**Materials.** Pyridine (Aldrich) was distilled from either calcium hydride or barium oxide and stored under nitrogen over potassium hydroxide. Cyclohexane (BDH Omnisolv) was distilled from sodium prior to use. Acetonitrile (BDH Omnisolv) was distilled under nitrogen after refluxing over calcium hydride for several days. Oxiranes and thiranes were commercial samples of the highest purity available (Aldrich) and were distilled prior to use. All other solvents and reagents were of the highest purity commercially available and were used as received.

**Diazirines (1).** 3-Benzyl-3-chlorodiazirine (**1a**) and 3-phenyl-3-chlorodiazirine (**1b**) were prepared by Graham oxidations and charac-

terized as described previously.<sup>57</sup> 3-Methoxy-3-phenyldiazirine (**1c**) was prepared by the exchange reaction of 3-bromo-3-phenyldiazirine with sodium methoxide in dimethylformamide (DMF) and characterized as described previously.<sup>9b,57</sup>

**$\Delta^3$ -1,3,4-Oxadiazolines (6).** Oxadiazolines were prepared by oxidative cyclization of the appropriate hydrazones using lead tetraacetate as described previously.<sup>28a</sup> The products were purified by column chromatography on silica gel with hexane/ethyl acetate (24:1) as eluents. Yields were determined from hydrazones.

**2,2-Dimethoxy-5,5-dimethyl- $\Delta^3$ -1,3,4-oxadiazoline (6a).**<sup>27</sup> Yield 70%, clear oil. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.53 (s, 6 H), 3.45 (s, 3 H). <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>)  $\delta$ : 23.7, 51.5, 118.8, 137.0. IR (neat, KBr): 2982, 2949, 2887, 2847, 1577, 1459, 1448, 1376, 1137, 1078, 930, 862 cm<sup>-1</sup>. MS (EI) *m/z*: (molecular ion not observed), 129 [M - OMe]<sup>+</sup>, 105, 91, 90, 75, 74, 73, 59 (100%), 43. MS (CI, NH<sub>3</sub>) *m/z*: 178 [M + NH<sub>4</sub>]<sup>+</sup>. UV (pentane):  $\lambda_{\text{max}}$  = 328 nm ( $\epsilon$  = 500).

**3,4-Diaza-2,2-dimethoxy-1-oxa[4.3]spirooct-3-ene (6b).** Yield 42%, clear oil. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.82–2.05 (m, 1 H), 2.10–2.38 (m, 1 H), 2.41–2.70 (m, 4 H), 3.29 (s, 6 H). <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>)  $\delta$ : 11.6 (+) (CH<sub>2</sub>), 31.0 (+) (CH<sub>2</sub>), 51.7 (–) (OCH<sub>3</sub>), 117.9 (+) (C), 138.2 (+) (C). IR (neat, KBr): 2990, 2951, 2847, 1565, 1443, 1240, 1122, 1071, 1031, 898, 823 cm<sup>-1</sup>. MS (EI) *m/z*: (molecular ion not observed), 141 [M - OMe]<sup>+</sup>, 117, 91, 74, 59 (100%), 54, 43. MS (CI, NH<sub>3</sub>) *m/z*: 190 [M + NH<sub>4</sub>]<sup>+</sup>. UV (pentane):  $\lambda_{\text{max}}$  = 328 nm ( $\epsilon$  = 500).

**5',5'-Dimethoxyspiro[adamantane]-2,2'-[ $\Delta^3$ -1,3,4-oxadiazoline] (6c).** Yield 56%, clear viscous oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.70–2.53 (m, 14 H), 3.44 (s, 6 H). <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>)  $\delta$ : 26.4 (–) (CH), 27.1 (–) (CH), 34.3 (+) (CH<sub>2</sub>), 34.7 (+) (CH<sub>2</sub>), 36.9 (+) (CH<sub>2</sub>), 51.6 (–) (OCH<sub>3</sub>), 124.2 (+) (C), 135.3 (+) (C). MS (EI) *m/z*: (molecular ion not observed), 221 [M - OMe]<sup>+</sup>, 165, 134, 119, 106, 105, 93, 92 (100%), 90, 79, 59. MS (CI, NH<sub>3</sub>) *m/z*: 270 [M + NH<sub>4</sub>]<sup>+</sup>. UV (pentane):  $\lambda_{\text{max}}$  = 328 nm ( $\epsilon$  = 300). Anal. Calcd for C<sub>13</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>: C, 61.88; H, 7.99; N, 11.10. Found: C, 61.60; H, 8.08; N, 10.71.

**Laser Flash Photolysis. UV–Vis.** The nanosecond laser system has been described previously.<sup>34</sup> Sample solutions were prepared with absorbances (A) of 0.3–0.6 at the excitation wavelength (355 or 308 nm) as described below. These solutions were contained in 7 × 7 mm quartz cells. A Lumonics HY750 laser (Nd:YAG, 355 nm, 10 ns pulses,  $\leq$ 40 mJ/pulse) and a Lumonics EX-530 excimer laser (XeCl, 308 nm, 6 ns pulses,  $\leq$ 40 mJ/pulse) were used.

**Diazirines 1.** The absolute rate constants for the reaction of carbenes **2a–c** with oxygen and sulfur atom donors were measured by UV-LFP. Stock solutions of diazirines **1** were prepared in freshly distilled cyclohexane and in freshly distilled acetonitrile so that  $A_{355}$  were approximately 0.2–0.6 depending on the precursor. Stock solutions of 1.0 M pyridine in cyclohexane and in acetonitrile were also prepared. The stock solution of diazirines **1a–c** were diluted by a factor of 2 in 2 mL cuvettes (so that  $A_{355} \approx 0.1–0.3$ ) with 1.0 M pyridine in cyclohexane and in acetonitrile, respectively. Solutions were degassed with N<sub>2</sub>, and the time-resolved UV–vis spectra were acquired (250–700 nm) after 355 nm LFP. Upon 355 nm LFP of diazirine **1a**, in the presence of pyridine, a long-lived absorption centered at  $\sim$ 370 nm was observed and assigned to the pyridine ylide **3a**, as well as an absorption centered at  $\sim$ 270 nm assigned to (*E*)- and (*Z*)- $\beta$ -chlorostyrenes.

For kinetic studies, stock solutions of diazirines **1a–c** were prepared in freshly distilled cyclohexane and in freshly distilled acetonitrile so that  $A_{355} \approx 0.2$  to 1.2. For diazirines **1a–c**, the stock solution was diluted by a factor of 2 (so that  $A_{308} \approx 0.6$ , 50 mL solutions) with various concentrations of pyridine in cyclohexane and in acetonitrile, respectively. These solutions were further diluted by a factor of 2 with solutions containing various concentrations of oxygen and sulfur atom

donors, purged with N<sub>2</sub>, and the time-resolved absorption traces (at 370 nm, or 480 nm) were acquired after 355 nm LFP.

**Oxadiazolines (5a–c).** Stock solutions of oxadiazolines **5a–c** were prepared in freshly distilled cyclohexane so that the  $A_{308}$  values were approximately 1.2. Typical concentrations of oxadiazolines required to accomplish this were  $\sim(2–3) \times 10^{-3}$  M. A stock solution of 1.0 M pyridine in cyclohexane was also prepared. For each oxadiazoline, stock solutions were similarly diluted by a factor of 2 with 1.0 M pyridine in cyclohexane (total volume 2 mL,  $A_{308} \approx 0.6$ ) and degassed with N<sub>2</sub>, and the time-resolved UV–vis spectra for each were acquired (300–700 nm) after 308 nm LFP.

Solutions of oxadiazolines **5a–c** ( $A_{308} = 1.2$ , path length 7 mm,  $(2–3) \times 10^{-3}$  M) were prepared containing 0.2 M pyridine in cyclohexane and diluted by a factor of 2 with solutions containing various amounts of oxiranes and thiiranes. Solutions were purged with N<sub>2</sub> prior to photolysis. The traces of these solutions were measured at 360 nm for carbenes **5a,b** and at 380 nm for carbene **5c**, after 308 nm-LFP, with data analysis as described for benzylchlorocarbene.

For each quenching experiment, UV–vis spectra were taken of solutions to ensure that the absorbances of the precursors **1** and **5a–c** at the excitation wavelength remained constant. Residual absorption of traps at the excitation wavelength can lead to errors in Stern–Volmer quenching, and concentration ranges were chosen to eliminate this possibility.

**Infrared.** For these experiments, samples contained in quartz flow cells with either 1 or 3 mm path lengths were excited at 308 nm with a Lumonics EX-530 excimer laser (XeCl, 308 nm, 6 ns pulses,  $\leq$ 40 mJ/pulse). The TRIR system has been described.<sup>40</sup>

**Steady-State Photolysis.** Steady-state photolyses were carried out in a Rayonet photochemical reactor equipped with a “merry-go-round” apparatus. Photolyses of benzylchlorodiazirine were performed in deoxygenated (N<sub>2</sub> or argon) solutions with 8–10 350 nm lamps. Oxadiazoline precursors were photolyzed in deoxygenated (N<sub>2</sub> or argon) solutions with 8–12 250 nm lamps and 1–2 300 nm lamps. Samples were prepared in either Pyrex or quartz tubes.

**Thermolysis of 5a.** Solutions of 0.1 M **5a** (0.0160 g in 1 mL) in benzene-*d*<sub>6</sub> were prepared containing 0.1 M cyclohexene oxide (0.009 81 g) or propylene sulfide (0.007 41 g). These solutions were placed into NMR tubes and degassed by means of three successive freeze–pump–thaw cycles, and the tubes were flame sealed. The sealed tubes were then heated at 110 °C in a constant temperature oil bath for 24 h. The resulting product mixtures were then analyzed by 500 MHz <sup>1</sup>H NMR spectroscopy. The seals were then broken and the reaction mixtures were analyzed by GC-MS.

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