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Photochemistry of 2,2,4,4-Tetramethyl-3-thietan-1-ylidene: A Heterocyclic Carbene with an Unusually Short Lifetime and Evidence for a Nonclassical Structure

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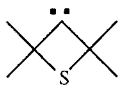
Laser flash (308 nm) and steady-state photolysis (300 nm) of Δ^3-1,3,4-oxadiazoline (**3**) produces a transient that can be trapped with pyridine to give an adduct with $\lambda_{max} = 350$ nm, attributed to ylide **10**. Laser flash photolysis (LFP) studies of the ylide indicate that the value of $k_{pyr}\tau$ (where k_{pyr} is the absolute rate constant of carbene reaction with pyridine and τ is the carbene lifetime) of the reactive intermediate is 25 times smaller than that deduced for cyclobutylidene. The sulfur-containing transient may have a much shorter lifetime than cyclobutylidene or a much smaller value of $k_{pyr.}$ These experimental results, along with ab initio calculations, suggest that the structure of 2,2,4,4-tetramethyl-3-thietan-1-ylidene is best represented as nonclassical, bisected structure **2** and not classical structure **1**.

Introduction

Cycloalkylidenes are of interest because of their ability to undergo a variety of reactions such as ring contraction[1] and intramolecular bond insertion.[2] Furthermore, the ground-state multiplicity of cycloalkylidenes is of fundamental interest because theory predicts that a singlet ground state is favored with decreasing ring size.[3]

Modern techniques such as time-resolved laser spectroscopy and computational methods have cast new light on the understanding of carbene chemistry, yet the effects of remote substituents such as heteroatoms on the properties and reactions of carbenes have received little attention. Our interest in the effects of heteroatom perturbation on the properties and reactions of cycloalkylidenes motivated this study, and herein we report the study of 2,2,4,4-tetramethyl-3-thietan-1-ylidene (**1**).



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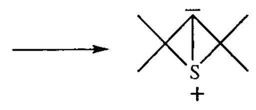

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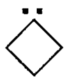


cyclobutylidene

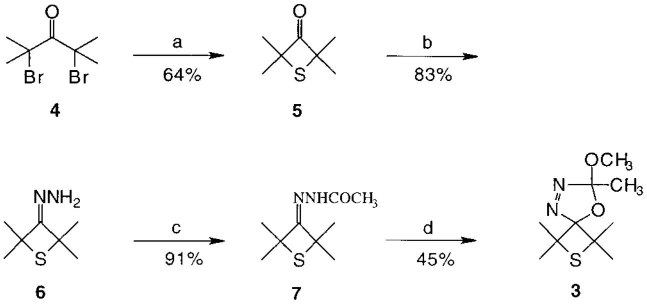
Carbene **1** is a sulfur analogue of cyclobutylidene.[1] Unlike cyclobutylidene, however, **1** may exist as an ylide, **2**, which represents a "nonclassical" form of the carbene. A similar type of structure has been proposed to describe the 3-thietan-1-yl cation,[4] and recent calculations suggest that even cyclobutylidene itself may have a "nonclassical" geometry.[5]

We are pleased to report that photolysis of oxadiazoline **3** (Scheme 1) provides entry into this system and that kinetic and computational evidence favors structure **2**, the nonclassical form of the carbene.

Experimental Section

General Procedures: Synthesis. All reactions were conducted in flame-dried glassware under an argon atmosphere. Solvents were dried prior to use by standard techniques. Reagents purchased from Aldrich were used as received. For the preparation of **5**, a cylinder of H_2S (Aldrich, 99.5+%) was used as received. Proton and carbon NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ using δ 7.26 and 77.0 ppm (center of triplet) as the reference peak for proton and carbon NMR, respectively. FT IR spectra were recorded between NaCl plates as CCl_4 solutions. GC/MS studies were recorded at an ionizing voltage of 70 eV. Where mass spectral data are given, the peak abundance immediately follows in parentheses. Elemental analysis of **7** was performed by Atlantic Microlab, Norcross, GA. *Caution*![6] *Because this preparation uses H_2S (toxic), it should be performed only in an efficient fume hood. Furthermore, since H_2S can spontaneously ignite as a 4−45% mixture with air, argon should be used as a bath gas to purge the system of air until the system is above the ignition volume of H_2S, and this purging should also be done when closing the flow of H_2S.*

SCHEME 1[a]



[a] Conditions: (a) H_2S, NaOMe/MeOH; (b) H_2NNH_2, HOAc, MeOH, 100 °C; (c) Ac_2O, DMAP, imidazole, CH_2Cl_2; (d) $Pb(OAc)_4$, MeOH/CH_2Cl_2, −10 °C.

The synthetic sequence is outlined in Scheme 1.

2,2,4,4-Tetramethyl-3-thietanone (5). To 16.0 g (0.314 mol) of NaOMe in 200 mL of MeOH was passed H_2S while maintaining the temperature of the solution below 15 °C. To this was added 50.0 g (0.184 mol) of 2,4-dimethyl-2,4-dibromo-3-pentanone (**4**) dropwise with continuous passage of H_2S while maintaining the solution temperature below 20 °C. After 3 h

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under H_2S, the solution was poured into 800 mL of water and extracted with Et_2O. The total Et_2O solution was dried over Na_2SO_4 and concentrated by rotary evaporation. Recrystallization of the white residue from MeOH gave 15.3 g of **5** as long, white needles. Spectral data was consistent with that previously reported. Mp = 104−106 °C (lit. mp = 106 °C).[7]

2,2,4,4-Tetramethyl-3-thietanone Hydrazone (6). In 75 mL of MeOH was placed 10.0 g (69.4 mmol) of **5**, 11.6 g (232 mmol) of hydrazine hydrate, and 0.80 g (13.3 mmol) of glacial acetic acid. The solution was refluxed at 100 °C for 5 days after which time the MeOH was removed by rotary evaporation. Recrystallization from 20% aqueous MeOH gave 9.2 g of **6**. Spectral data were consistent with that previously reported. Mp = 66−67 °C (lit. mp = 66 °C).[8]

2,2,4,4-Tetramethyl-3-thietanone Acetylhydrazone (7). To 9.2 g (58.2 mmol) of **6**, 0.28 g (2.3 mmol) of *p*-(dimethylamino)-pyridine (DMAP), and 6.5 g (96.0 mmol) of imidazole in 290 mL of CH_2Cl_2 was added dropwise 8.9 g (87.3 mmol) of acetic anhydride in 40 mL of CH_2Cl_2 over 30 min. After 4 h the mixture was washed with two 80 mL portions of water. The aqueous layer was extracted with 40 mL of CH_2Cl_2, and the total organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation to give a white solid. Three recrystallizations from MeOH gave 11.1 g of analytically pure **7** as fine white needles which begin to sublime at 192° C, mp (sealed capillary) = 197−199 °C. IR: 1692, 1667 cm^{-1}. H NMR: δ 1.65 (s, 6 H), 1.79 (s, 6 H), 2.21 (s, 3 H), 8.39 (broad s, NH) ppm. C NMR: δ 19.79, 29.27, 31.04, 52.95, 54.70, 159.91, 173.08 ppm. GC/MS: 202.00 (0.4) 126.05 (100), 125.05 (39), 11.05 (28), 43.00 (21). Anal.Calcd for **7**: C, 54.00; H, 8.00; N, 14.00; S, 16.00. Found: C, 54.06; H, 8.01; N, 13.95; S, 16.08.

7-Methoxy-1,1,3,3,7-pentamethyl-8-oxa-2-thia-5,6-diazaspiro[3.4]oct-5-ene (3). To 16.0 g (36.1 mmol) of $Pb(OAc)_4$ in 150 mL of MeOH cooled to −8 °C was added dropwise 6.0 g (30.0 mmol) of **7** in 40 mL MeOH and 60 mL CH_2Cl_2 over 3 h while the solution temperature was maintained between −8 and −6 °C. After 4.5 h with warming of the solution to between 10 and 15 °C, followed by 2 h at 20 °C, the solution was cooled to −8 °C and 2.3 g KOH in 25 mL MeOH was added dropwise such that the solution temperature was maintained between −8 and −7 °C. After 8 h, the MeOH was removed by rotary evaporation, the white residue was taken up in 300 mL CH_2Cl_2 and washed with three 100 mL portions of water, and the organic layer was dried over Na_2SO_4. Following removal of the CH_2Cl_2 by rotary evaporation, silica gel column chromatography using 5:1 pentane−Et_2O ($R_f = 0.62$) as the eluant gave 3.1 g of **3** as a clear, colorless liquid. IR: 3083, 3004, 2941, 2858 cm^{-1}. H NMR: δ 1.52 (s, 6 H), 1.54 (s, 6 H), 2.10 (s, 3 H, CH_3), 3.13 (s, 3H, $-OCH_3$) ppm. GC/MS: 202 [M^+ (−N2) (3)], 128 (100), 113 (69), 95 (44), 85 (77), 59 (36), 43 (75). UV (pentane): $\lambda_{max} = 232, 336$ nm.

Steady-State Photolysis (300 nm) of 3 in C_6H_{12}. Into a quartz cuvette was placed 10.0 mg of **3** (0.043 mmol) in 1.0 mL of cyclohexane. The cuvette was capped with a rubber septum, and then the solution was purged with argon for 5 min, followed by irradiation with 300 nm light (Ray-o-Net reactor) at 5 °C for 3 h. Analysis of the mixture by GC/MS showed that azine **9** and sulfide **11** were formed. There was no evidence for the formation of an adduct with cyclohexane (e.g., **12**) The mass spectrum of **11** was consistent with that previously reported.[9]

Steady-State Photolysis (254 nm) of 3 in C_6H_{12}. Into a quartz cuvette was placed 10.0 mg of **3** (0.043 mmol) in 1.0 mL of cyclohexane. The cuvette was capped with a rubber septum, and then the solution was purged with argon for 5 min, followed by irradiation with 254 nm light (Rayonet reactor) at 5 °C for 3 h. Analysis of the mixture by GC/MS showed that thietanone **5** had been formed, but neither **9** nor **11** nor **12** could be detected in the product mixture.

LFP Studies: General Procedures. The cyclohexane used in the LFP studies was distilled from sodium and stored over 4 Å molecular sieves. Cyclohexane-d_{12} (CIL, 99.7%) was used as received. Pyridine was distilled and stored over 4 Å molecular sieves. Freon-113 (Aldrich, HPLC grade) was passed through a column of alumina immediately prior to use. For Stern−Volmer kinetics, 1-hexene, 2,3-dimethyl-2-butene, cyclohexene, and acrylonitrile were passed through a column of alumina immediately prior to use.

LFP Studies: Kinetics. A stock solution of **3** was prepared to an optical density of 0.55 at 308 nm in the appropriate solvent, and 1.0 mL of this solution was added to quartz cuvettes. To each cuvette a specific amount of pyridine was added, and then an appropriate amount of solvent such that the total volume in each cuvette was 2.0 mL. Each cuvette was then capped with a rubber septum, wrapped in foil, and degassed by purging with dry, oxygen-free argon for 5 min immediately prior to LFP at 308 nm. Three transient spectra were recorded for each cuvette, and averaged transient A_{350} values were used in the data analysis. In the lifetime experiments, the pyridine concentration was typically varied from 0.1 to 3.0 M for a series of 12−15 cuvettes.

Stern−Volmer quenching experiments were performed by adding 1.0 mL of the Freon-113 stock solution of **3** used in the lifetime experiments containing 3.0 M in pyridine to quartz cuvettes. To each cuvette was then added a specific amount of olefin, and then an appropriate amount of Freon-113 was added such that the total volume in each cuvette was 2.0 mL. Each cuvette was then capped with a rubber septum, wrapped in foil, and degassed by purging with dry, oxygen-free argon for 5 min immediately prior to LFP at 308 nm. Three transient spectra were recorded for each cuvette, and average A_{350} values were used in the data analysis. For a given olefin, the range of quencher concentration was typically varied between 0.00 and 1.0 M for a series of 8−10 cuvettes. The spectrometer has been described previously.[10]

General Procedures: Calculations. All molecular geometries were fully optimized using GAUSSIAN 94[11] and the frozen-core approximation.[12]

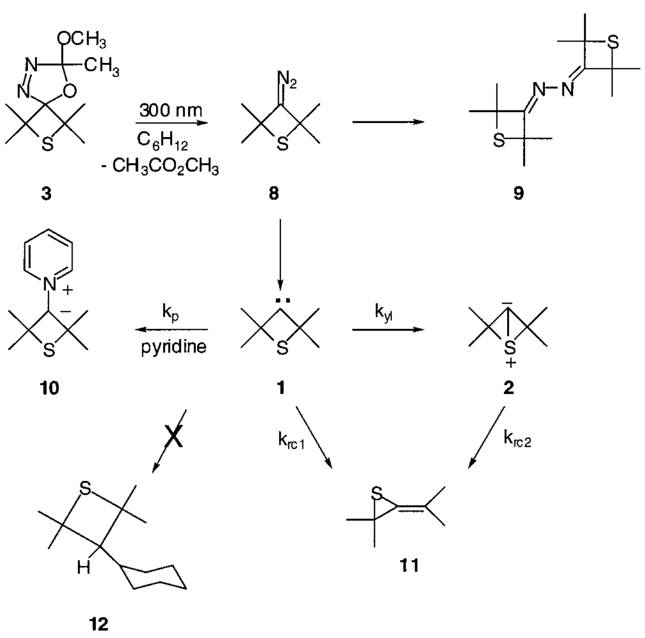
Results and Discussion

Synthesis of the Precursor

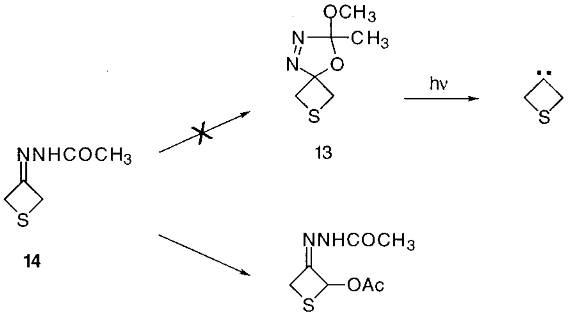
The first task at hand was the preparation of a precursor that cleanly yields a thiocyclobutylidene upon photolysis. It has been shown that diazirines are frequently inefficient precursors to carbenes, as products are often derived from excited-state reactions of the diazirine or from a biradical resulting from C−N bond cleavage.[13] Also, small-ring spiro diazirines are sometimes difficult to synthesize in good yield and to handle in a pure state.

Oxadiazolines are quite often efficient carbene precursors and are easy to prepare and handle.[14] We initially directed our attention toward the preparation of an oxadiazoline precursor (**13**) to the unsubstituted sulfur analogue of cyclobutylidene, but treatment of acetylhydrazone **14** with $Pb(OAc)_4$ did not lead to the desired **13** but rather to incorporation of an acetoxy group adjacent to sulfur. The replacement of hydrogen α to sulfur by OAc with $Pb(OAc)_4$ has been reported.[15] To block this process, we next turned our attention to the preparation of tetramethyl

SCHEME 2



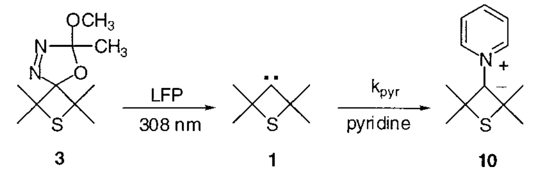
derivative **3**, as described in Scheme 1. Owing to the poor yields of **7** obtained from reaction of **5** with acetic hydrazide, even under stringent conditions such as in glacial acetic acid at 100 °C, **7** was prepared stepwise from **5** in good yield.



Photochemistry

Steady-state photolysis (Ray-o-Net) of **3** in degassed cyclohexane at 300 nm followed by GC/MS analysis of the resulting mixture showed that one product had a cracking pattern consistent with that of **11** (Scheme 2), which has been reported as a product from the pyrolysis of the tosylhydrazone salt derived from **5**.[9] It is interesting to note that **11** is only one of two allene episulfide derivatives known, the other being a perfluorinated derivative.[16] The second product observed from the photolysis of **3** had strong peaks in the mass spectrum at *m*/*z* of 284 and 142, which are attributed to the azine, **9**. The azine is most likely derived from the diazo intermediate **8**, which is initially formed by fragmentation of **3**. None of the other possible photoproducts from **3**, such as that from insertion into the C−H bonds of cyclohexane solvent, were detected.

Laser flash photolysis (LFP, 308 nm, XeCl) of **3** in 1,1,2-trifluorotrichloroethane (Freon-113) did not produce detectable transient absorption. In the presence of pyridine, however, a transient with $\lambda_{max} = 350$ nm, attributed to that of ylide **10** was observed (Figure 1). As postulated (vide supra), **1** may exist as ylide-type structure **2**. This ylide was not detected as shown in Figure 1 (curve A). Although this is a negative result, the failure to detect **2** may reflect the fact that **2** has a poor chromophore. Evidence will be presented (vide infra) that supports **2** as the structure of the transient intermediate.



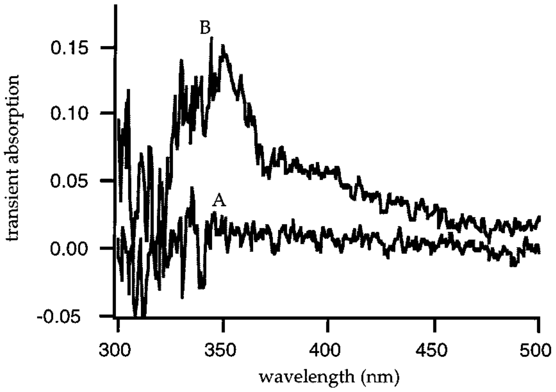


Figure 1. Transient spectrum obtained following LFP of oxadiazoline **3** in Freon-113 containing the following: A, 0.00 M pyridine; B, 2.48 M pyridine. The spectra were recorded over a time window of 250 ns, 50 ns following the laser flash.

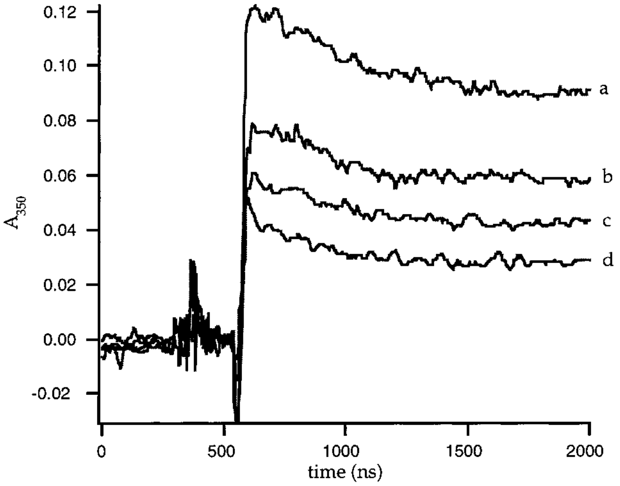


Figure 2. Formation and decay of **10** in Freon-113 containing the following pyridine concentrations: a, 2.48 M; b, 1.12 M; c, 0.62 M; d, 0.37 M. The spectra were recorded over a time window of 2000 ns.

Ylide **10** was formed faster than the time resolution (≈20 ns) of the spectrometer (Figure 2); thus, it was not possible to measure the lifetime of **1** by measurement of the growth of ylide **10**. Measurement of the absorption at 350 nm as a function of pyridine concentration, however (Figures 2 and 3), revealed that when [pyridine] > 2.5 M, the optical yield of **10** did not increase.

This implies that every intermediate generated by the laser pulse is trapped by pyridine to form **10** when [pyridine] > 2.5 M. The lifetime of the intermediate generated from the photolysis of **3** may be deduced from the data in Figure 3. Double reciprocal treatment of the data in Figure 3 is predicted and found to be linear (Figure 4).[17] Division of the intercept by the slope of Figure 4 yields $k_{pyr}\tau$, and using $k_{pyr} = 1 \times 10^9 - 5 \times 10^9$ M^{-1} s^{-1}, which is a typical range for reaction of singlet carbenes with pyridine,[18] the deduced lifetime of the intermediate in Freon-113 is found to be 0.2−0.8 ns (Table 1). It is interesting to note that the lifetime of **1**/**2** is considerably shorter than that deduced for cyclobutylidene (4−20 ns) in Freon-113,

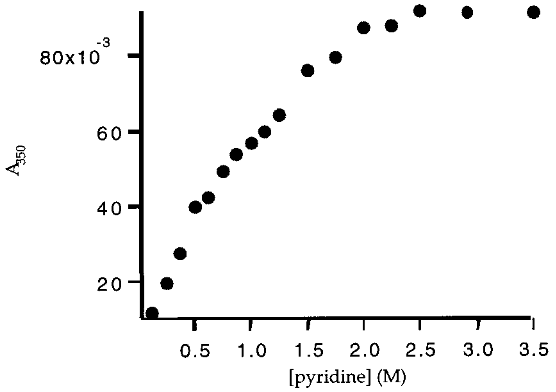


Figure 3. Optical yield of ylide **10** produced by LFP of **3** measured at 350 nm (A_{350}) vs [pyridine] in Freon-113.

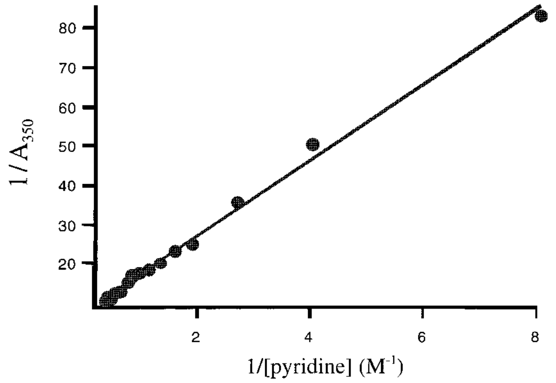


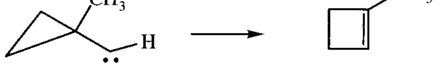
Figure 4. Double reciprocal treatment of the data in Figure 3.

TABLE 1: Deduced Lifetimes of Singlet 1/2

solvent	$k_{pyr}\tau$	τ (ns)
$CF_2ClCFCl_2$	0.8	0.2−0.8
cyclohexane	0.7	0.1−0.7
cyclohexane-d_{12}	0.7	0.1−0.7

C_6H_{12}, and C_6D_{12} by the same method.[19] However, **1**/**2** may not be a typical carbene and may have a value of k_{PYR} lower than $1 \times 10^{-9} - 5 \times 10^{9}$ M^{-1} s^{-1}. This would increase the deduced lifetime of **1**/**2**.

It is also noteworthy that the lifetime of **1**/**2** in cyclohexane is essentially the same as in cyclohexane-d_{12} (Figure 5). Thus, there is no solvent isotope effect on the lifetime of **1**/**2** in C_6H_{12} or C_6D_{12}. This suggests that **1**/**2** does not appreciably form products from C−H(D) insertion with solvent, which is consistent with the results obtained from steady-state photolysis of **3** in cyclohexane solvent in which no products resulting from C−H insertion of **1**/**2** were detected by GC/MS. The lifetime of **1**/**2** in cyclohexane is controlled by intramolecular rearrangement. Thamattoor et al. have shown that a methyl substituent will accelerate carbon-bond migration in cyclopropylcarbene.[20]



Thus, it is possible that the *gem*-dimethyl substitution in **1**/**2** accelerates bond migration relative to cyclobutylidene.

Of particular issue in the use of oxadiazolines as carbene precursors is their ability to fragment by an alternative mode to yield methoxy(methyl)carbene. In the case of precursor **3**, this would yield the ketone **5**. This product was not detected upon 300 nm (Ray-o-Net) steady-state photolysis of **3**. Methoxy(methyl)carbene is a relatively long-lived carbene.[21] The fast (τ < 20 ns) formation of **10** and the short deduced lifetimes of the transient intermediate derived from **3** (Table 1) do not support the generation of methoxy(methyl)carbene. It is interesting to note, however, that when the steady-state photolysis was performed at 254 nm (Ray-o-Net), GC/MS analysis revealed that **5** was indeed formed. Thus, the mode of fragmentation of **3** is wavelength dependent. Wavelength-dependent photochemistry of oxadiazolines has been reported previously.[22]

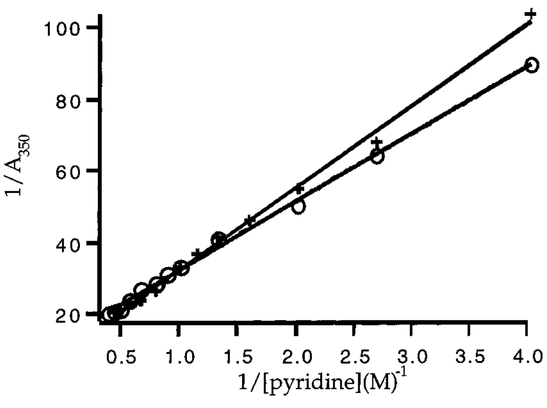


Figure 5. Double reciprocal plot for calculation of the lifetime of **1** in (○, - - -) C_6D_{12} and (+, —) C_6H_{12}.

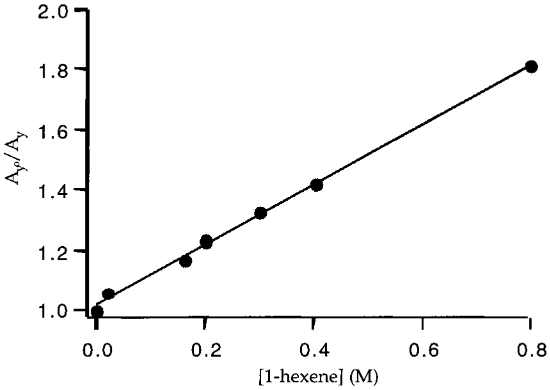
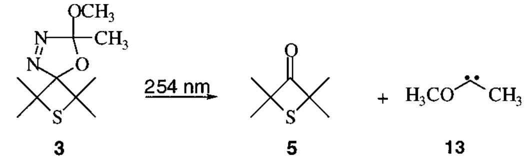


Figure 6. Stern−Volmer plot for quenching of **10** with [1-hexene] at [pyridine] = 3.0 M in Freon-113.



It was of interest to determine the absolute (and therefore relative) rate constants for reaction of **1**/**2** with olefins. In the case of **1**/**2**, eq 1 is valid when [pyridine] > 2.5 M.[17]

$$\frac{A_y^{0}}{A_y} = \frac{1 + k_{olefin}[olefin]}{k_{pyr}[pyridine]} \qquad (1)$$

Thus, LFP of a Freon-113 solution of **3** containing [pyridine] = 3.0 M in the presence of an olefin quencher is expected to reduce the absorption of ylide, A_y^{o}, at infinite pyridine concentration[17] as the concentration of olefin increases. This is exactly what is observed as shown in Figure 6 for 1-hexene. As may be expected for a short-lived intermediate, the spread of reactivity of **1**/**2** for reaction with the olefins of this study is not large. Nonetheless a trend in reactivity exists. The most

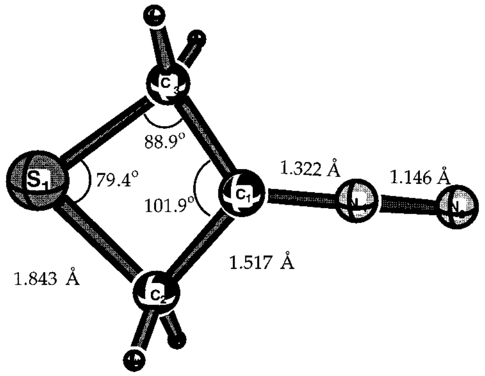


Figure 7. Geometry of diazo compound **8** optimized at the MP2/6-311+G** level of theory.

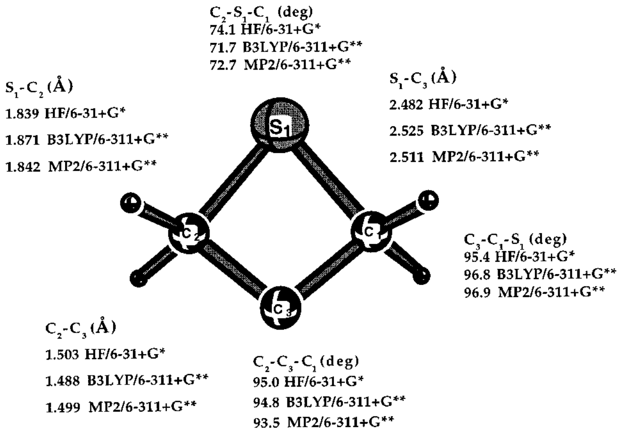


Figure 8. Geometry of **1** optimized at the MP2/6-311 + G** level of theory.

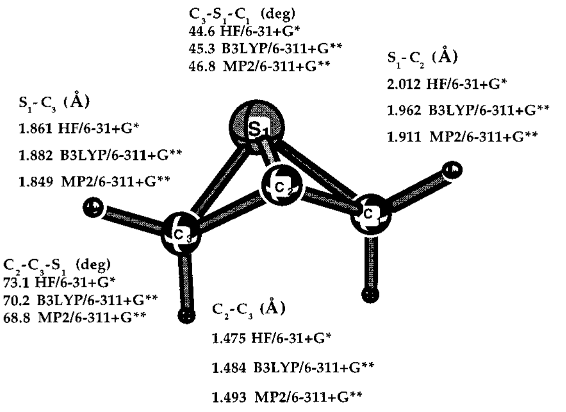


Figure 9. Geometry of **2** optimized at the MP2/6-311+G** level of theory.

electron-poor olefin, acrylonitrile, reacts nearly twice as rapidly with **1**/**2** as does the most electron-rich olefin, 2,3-dimethyl-2-butene. One may attribute this to a steric effect, as the methyl groups of 2,3-dimethyl-2-butene may make addition of **1**/**2** to the double bond more difficult than in either 1-hexene or acrylonitrile, in which the double bond is relatively unhindered. However, if the k_{rel} data are solely due to a steric effect, then 1-hexene would be expected to react with **1**/**2** at nearly the same rate as it does with acrylonitrile instead of 26% more slowly. One might also expect that **1** would react more slowly with acrylonitrile as compared to 1-hexene, as the classical structure of **1** would resemble a typical electrophilic carbene.[23] This suggests that the structure of the transient may be nonclassical structure **2**, which appears nucleophilic as written.

TABLE 2: Stern−Volmer Analysis for Rate of Reaction of 1/2 with Olefins

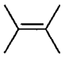
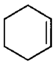
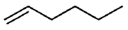
Olefin	k_{olefin} (M^{-1} s^{-1})^a	k_{rel}
	3.1×10^9	1.00^b
	3.5×10^9	1.1
	4.3×10^9	1.4
	5.7×10^9	1.9

TABLE 3: Relative Energies (kcal/mol) of Structures 1 and 2

method	$E_2 - E_1$
HF/6-31+G*	−7.4
B3LYP/6-311+G**	−15.6
MP2/6-311+G**	−25.3
CCSD(T)/DZP//MP2/6-311+G**	−60.6

Computational Chemistry

It was of interest to examine the structures **1** and **2** by ab initio molecular orbital theory. To simplify the calculations, the unsubstituted parent structures of **1** and **2** were optimized using HF,[12] B3LYP,[24] and MP2[25] levels of theory. Since the 300 nm steady-state photolysis suggests that diazo compound **8** is the immediate precursor to **1**/**2**, diazo compound **8** was optimized at the MP2/6-311+G** level of theory, and the ring was found to have a puckering or flap angle of 10°.

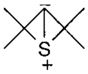
Removal of the N_2 group from the optimized structure **8** served as the starting point to determine what type of geometry this initial structure would adopt. Geometry optimization at the HF, B3LYP, and MP2 levels of theory revealed that the stationary point was that of nonclassical structure **2**, which was lower in energy than **1** at all levels of theory examined (Table 3). Frequency calculations at the B3LYP/6-311+G** level of theory on the structures **1** and **2** optimized at this same level showed that **2** is a minimum, with **1** being characterized by an imaginary frequency. Thus, the calculations suggest that **1** and **2** are not in equilibrium with each other and that **1** is a transition state. Furthermore, positive and negative charge in **2** is concentrated at S_1 (+0.183) and C_2 (−0.145), and nonclassical structure **2** has a dipole moment of 2.8 D.

Although at the expense of increasing angle strain, four-membered rings are known to adopt "puckered" conformations in order to alleviate eclipsing strain between adjacent bonds.[26] The puckering angle would be zero degrees if both cyclopropane rings of a [1.1.0] ring system were coplanar. It was of interest to compare the "puckered" geometry of **2** with bicyclo[1.1.0]-butane,[27] which is an experimentally known all-carbon analogue of **2**. The geometry of bicyclo[1.1.0]butane was optimized at the same levels of theory employed in the study of **2**. Although the presence of sulfur in the ring of **2** prohibits any comparison of bond lengths and angles between **2** and bicyclo[1.1.0]butane, Table 4 shows that **2** has a puckered geometry that very much resembles bicyclo[1.1.0]butane. The puckering angles of these two ring systems are very different from that of cyclobutane, which is 22°.[28]

Conclusions

The LFP (308 nm) and steady-state (300 nm) studies of this work are consistent with the generation of an intermediate from oxadiazoline precursor **3**. This intermediate can be trapped with pyridine to give a transient with λ_{max} = 350 nm, attributed to that of ylide **10**. Ab initio calculations at different levels of

TABLE 4: Calculated Puckering Angles of 2 and Bicyclo[1.1.0]butane

Theory	 **2**	 **bicyclo[1.1.0]butane**
HF/6-31+G*	61.8	59.0
B3LYP/6-311+G**	64.5	58.0
MP2/6-311+G**	66.5	57.3

theory indicate that **2** is lower in energy than **1** and that the latter structure is characterized by an imaginary frequency. The classical structure of carbene **1** is a transition state. Thus, theory suggests that **1** and **2** are not in equilibrium and that the intermediate generated by the photolysis of **3** is **2**. The lifetime of **2** in C_6H_{12} is essentially the same in C_6D_{12} and indicates that **2** does not undergo C−H(D) insertion with solvent. This is supported by the 300 nm steady-state photolysis results in which insertion products were not detected. The lifetime of **2** in Freon-113, C_6H_{12}, and C_6D_{12} is about 25 times shorter than that deduced for cyclobutylidene. The shorter lifetime deduced for intermediate **2** as compared to cyclobutylidene may be an artifact. If **2** is the true structure of the intermediate, then the lone pair of electrons on the nitrogen of pyridine would have to attack a carbon with a formal negative charge to give adduct **10;** thus the actual k_{pyr} value may be considerably smaller than the typical value of $1 \times 10^9 - 5 \times 10^9$ M^{-1} s^{-1} used here to deduce the lifetime of cyclobutylidene and a reduction of k_{pyr} will lead to an increase in τ.[17]

Due to the rigid nature of the four-membered ring, the large sulfur atom in **1** is ideally situated to donate an electron pair to the carbene center to give **2**. Thus, the photoproduct **11** may result from rearrangement of **2**. Furthermore, Stern−Volmer analysis showed that acrylonitrile and 1-hexene react most rapidly with **2** and this is likely due to a steric effect. It was found, however, that acrylonitrile reacts 26% more rapidly than does 1-hexene with **2**. This is not what one may predict for classical carbene structure **1** which is expected to be electrophilic. The data are consistent with nonclassical structure **2**, which is expected to be nucleophilic.

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