J. Am. Chem. Soc. **2001,** *123,* 6061−6068

Carbomethoxychlorocarbene: Spectroscopy, Theory, Chemistry and Kinetics

Igor Likhotvorik, Zhendong Zhu, Eunju Lee Tae, Eric Tippmann, Brian T. Hill, and Matthew S. Platz*

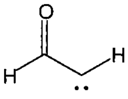
Contribution from the Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210

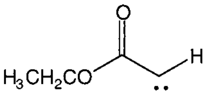
Received December 11, 2000. Revised Manuscript Received May 2, 2001

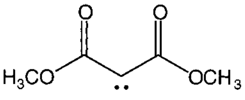
Abstract: Photolysis (254 nm) of methyl 8-chloro-3a,7a-methanoindan-8-carboxylate (**5**) in argon at 14 K produces carbomethoxychlorocarbene (**6**) as a persistent species. The IR and UV−vis spectra of the carbene were recorded and analyzed with the aid of density functional calculations (B3-LYP/6-31G*). The IR spectrum of **6** is consistent with the carbene having a nonplanar singlet ground state, in agreement with the G3(MP2)//B3-LYP calculations of Scott and Radom (accompanying paper). Irradiation (300 nm) of **5** in solution produces indane in 97% yield. In cyclohexane, carbene **6** is trapped by insertion into a CH bond, whereas in 2,3-dimethylbutene it adds to the double bond to form a cyclopropane. Laser flash photolysis of **5** (308 nm, 17 ns, XeCl excimer) produces carbene **6** which reacts with pyridine to form an ylide ($\lambda_{max} = 440$ nm). It was possible to resolve the growth of the ylide in Freon-113 ($CF_2ClCFCl_2$) to measure the lifetime ($\tau = 114$ ns, ambient temperature) of the carbene and the absolute rate constant of its reaction with pyridine ($k_{pyr} = 2 \times 10^9$ M^{-1} s^{-1}). A plot of log($1/\tau$) versus $1/T$ in $CF_2ClCFCl_2$ is linear with Arrhenius parameters $E_a = 10.9 \pm 0.8$ kJ/mol and $A = 10^{9.1\pm0.2}$ s^{-1}. In perfluorohexane, a less reactive solvent than Freon-113, $E_a = 23.4 \pm 1.7$ kJ/mol, $A = 10^{10.6\pm0.}$ s^{-1}, and $\tau = 354$ ns at 293 K. It is argued that the activation barrier to carbene disappearance in perfluorohexane represents the lower limit to the barrier to Wolff rearrangement of the carbene.

I. Introduction

Carbonylcarbenes are widely used in synthesis and are easily generated.[1] Consequently, the simplest examples such as **1**−**3** have been extensively studied by classical methods. The lifetimes of **1**−**3** in Freon-113 and in cyclohexane are controlled by intramolecular Wolff rearrangement (WR) and are ≈1 ns at ambient temperature.[2−4] The short lifetimes of **1**−**3** in solution prevented direct measurement of the Arrhenius parameters of the WR of these carbenes by nanosecond spectroscopy.


1


2


3

The ground states of simple carbonyl carbenes are predicted by theory to have triplet multiplicity and to be planar.[5−8] On the other hand, the lowest singlet states of the carbonyl carbenes are predicted to be nonplanar with closed shell configurations.[5−8] Formyl carbene has not been generated as a persistent species in a low-temperature matrix.[9] Triplet carbomethoxycarbene, however, has been detected by ESR spectroscopy at low temperature.[10] This carbene has not been observed by matrix IR and UV−vis spectroscopy because these techniques have lower sensitivity than ESR spectroscopy.[9] A 20 year old calculation of Kim and Schaefer indicates that the triplet state of carbohydroxycarbene is 29.3 kJ/mol more stable than the singlet. A more recent calculation of Xie and Schaefer predicts a triplet−singlet spliting of 19.7 kJ/mol.[6] Thus, the interpretation of time-resolved experiments of simple carbonyl carbenes is complicated by the fact that the ground states of carbenes **1**−**3** have triplet spin multiplicity,[5−8] but WR proceeds through the closed shell singlet state.[11]

Aryl carbonyl carbenes have triplet ground states and have been characterized in low-temperature matrices by ESR, UV−vis, and IR spectroscopy.[9,12] The aryl group stabilizes the singlet

---

(1) (a) Rodina, L. L.; Korobitsyna, I. K. *Russ. Chem. Rev.* **1967**, *36*, 260. (b) Marchand, A. P.; Brockway, N. M. *Chem. Rev.* **1974**, *74*, 431. (c) Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32. (d) Toscano, J. P. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 7, p 215.

(2) (a) Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Cao, Y.; Zimmt, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 3527. (b) Toscano, J. P.; Platz, M. S.; Nikolaev, V. *J. Am. Chem. Soc.* **1995**, *117*, 4712.

(3) Toscano, J. P.; Platz, M. S.; Nikolaev, V. *J. Am. Chem. Soc.* **1994**, *116*, 8146.

(4) Wang, J.-L.; Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popik, V. *J. Am. Chem. Soc.* **1995**, *117*, 5477.

(5) (a) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333. (b) Tanaka, K.; Yoshimine; M. *J. Am. Chem. Soc.* **1980**, *102*, 7653. (c) Harding, L. B.; Wagner, A. F. *J. Phys. Chem.* **1987**, *91*, 6484. (d) Gosavi, R. K.; Torres, M.; Strausz, O. P. *Can. J. Chem.* **1991**, *69*, 1630.

(6) (a) Kim, K. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1980**, *102*, 5389. (b) Xie, Y.; Schaefer, H. F., III *Mol. Phys.* **1996**, *87*, 389−397.

(7) Vacek, G.; Galbraith, J. M.; Yamaguchi, Y.; Schaefer, H. F., III; Nobes, R. H.; Scott, A. P.; Roden, L. *J. Phys. Chem.* **1994**, *98*, 8660.

(8) Scott, A.; Radom, L. *J. Am. Chem. Soc.* **2001**, *123*, 6069−6076.

(9) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583.

(10) Hutton, R. S.; Roth, H. D. *J. Am. Chem. Soc.* **1978**, *100*, 4321.

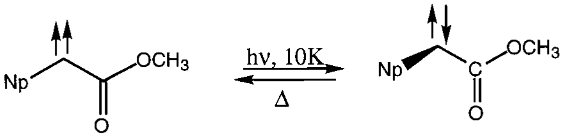
(11) Scott, A. P.; Nobes, R. H.; Schaefer, H. F., III; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 10159.

(12) (a) Fujiwara, Y.; Tanimoto, Y.; Itoh, M.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **1987**, *109*, 1942. (b) McMahon, R. J.; Chapman, O. L.; Hayes, R. D.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597. (c) Hayes, R. A.; Hess, T. C.; McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1983**, *105*, 7786.

10.1021/ja004235m CCC: $20.00

state of the carbene which allows relaxation to the triplet state to compete with WR.

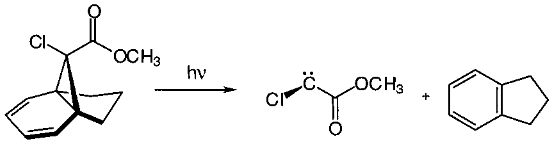
Photolysis of matrix isolated planar triplet carbene **4T** produces orthogonal singlet carbene **4S** (Np = 2-naphthyl). A small intrinsic barrier, enhanced perhaps by frictional forces in the matrix, prevents rapid relaxation of **4S** to **4T**. This allows the low-lying singlet **4S** to be characterized by IR and UV−vis spectroscopy in frozen argon.[13] This is the only case in which *both* the lowest singlet and triplet states of a carbene have been studied by matrix spectroscopy.[13]



4T **4S**

The equilibrium constant $K = \mathbf{4S}/\mathbf{4T}$ was measured by Toscano et al. by TRIR spectroscopy in liquid $CF_2ClCFCl_2$ (Freon-113) and is approximately 0.7 ($\Delta G_{ST} = 0.2$) at ambient temperature.[14] The barrier to disappearance of the spin equilibrated carbene (**4S**, **4T**) in Freon-113, presumably by Wolff rearrangement, is 14.2 kJ/mol.[15] Again, this result is difficult to interpret because the triplet is the ground state and the rearrangement proceeds on the singlet surface.[11,14,15]

Herein, we are pleased to report that photolysis of 8-chloro-3a,7a-methanoindane-8-carboxylate (**5**) produces carbomethoxychlorocarbene (**6**). The chlorine substituent differentially stabilizes the singlet state and renders the singlet as the ground state.[16] Chlorine, as aryl substitution kinetically stabilizes the singlet carbene[17] and allows for direct observation and study of the chemistry and spectroscopy of this carbene by a variety of techniques. It also allows a straightforward mechanistic analysis of the kinetics of disappearance of a singlet carbonylcarbene in solution without having to consider the influence of spin state equilibration.



5 **6**

II. Results

II.1. Synthesis. Jones' dichloride **7** has been shown to be a convenient photochemical source of dichlorocarbene.[18] This compound was treated with *n*-butyllithium in THF at −78 °C to form an organometallic reagent we will designate as **8** in the interest of simplicity. Pouring **8** onto dry ice followed by treatment with methyl iodide formed **5** in 65−76% yield (from **7**).

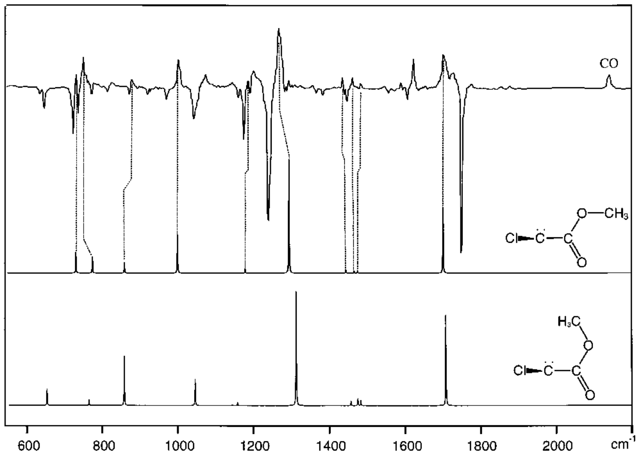
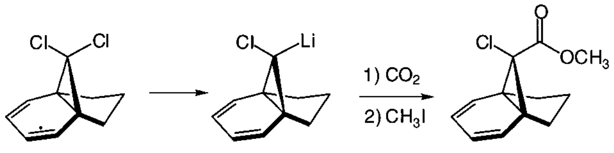


Figure 1. The IR difference spectrum obtained after 254 nm photolysis of **5** in an Ar matrix at 12 K (top). IR spectra of the two singlet carbene conformers, *Z*-^{1}**6** (middle) and *E*-^{1}**6** (bottom), calculated at the B3LYP/6-31G* level (all frequencies scaled by 0.97).



7 **8** **5**

II.2. Matrix Isolation Spectroscopy. Compound **5** was deposited in argon at 14 K and its IR and UV−vis spectra were recorded. It was then irradiated at 254 nm (Ray-O-Net) and spectra were obtained at different intervals. Upon photolysis, the IR bands of **5** (1750, 1243, 1178, 1047, 742, 728, and 652 cm^{-1}) are reduced and prominent bands at 1270, 1007, and 757 cm^{-1} as well as a single, broad carbonyl band centered 1702 cm^{-1} appear in the IR spectrum (Figure 1). Carbon monoxide (2139 cm^{-1}) is also produced upon photolysis (254 nm) of **5**. One of the anticipated products of photolysis of **5** is indane. Thus, indane was independently deposited in argon and its vibrational spectrum was recorded (Figure S7 in the Supporting Information). The two largest bands in the IR spectrum of indane are observed at 738 and 751 cm^{-1}. It is difficult to identify these two bands conclusively in the spectrum obtained upon photolysis of **5**, because of the disappearance of the precursor band at 742 cm^{-1}. It is clear, however, that while indane may contribute to the photoproduct band at 757 cm^{-1}, the prominent photoproduct bands observed at 1702, 1270, and 1007 cm^{-1} are not due to indane and must originate from another species.

A weak broad band appears at 640 nm in the visible region along with a stronger band at 320 nm in the ultraviolet region of the spectrum (Figure 2). These two absorption bands are formed under the same photolysis conditions which lead to the changes observed in the IR spectra of Figure 1.

The vibrational bands at 1702, 1270, and 1007 cm^{-1} together with the electronic absorptions at 320 and 640 nm will be attributed to singlet carbomethoxychlorocarbene **6** on the basis of the calculations presented in Section II.3 as well as their behavior upon photolysis and in the presence of carbon monoxide. Furthermore, it will be shown that the IR spectrum is consistent with the presence of a single conformer of the carbene, the lowest energy (*Z*-conformation) of **6** in the matrix.

---

(13) Zhu, Z.; Bally, T.; Stracener, L.; McMahon, R. *J. Am. Chem. Soc.* **1999**, *121*, 2863.

(14) Wang, Y.; Yuzawa, T.; Hamaguchi, H.; Toscano, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 2875.

(15) Wang, J.-L.; Likhotvorik, I.; Platz, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 2883.

(16) (a) Carter, E. A.; Goddard, W. A., III. *J. Chem. Phys.* **1988**, *88*, 1752. (b) Shin, S. K.; Goddard, W. A., III; Beauchamp, J. C. *J. Chem. Phys.* **1990**, *94*, 6963. (c) Murray, K. K.; Leopold, D. G.; Miller, T. M.; Lineberger, W. C. *J. Chem. Phys.* **1988**, *89*, 5442.

(17) (a) Bucher, G.; Scaiano, J. C.; Platz, M. S. *Kinetics of Carbene Reactions in Solution*, Landolt-Bornstein, Group II, Vol. 18, Subvolume E2; Springer: Berlin, Germany, 1998; p 141. (b) Ge, C.-S.; Eun, G. J.; Jefferson, E. A.; Liu, W.; Moss, R. A.; Wlostowska, J.; Xue, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1479. (c) Moss, R. A. *Pure Appl. Chem.* **1995**, *67*, 741.

(18) Hartwig, J. F.; Jones, M., Jr.; Moss, R. A.; Lawrynowicz, W. *Tetrahedron Lett. **1986***, 27, 5907.

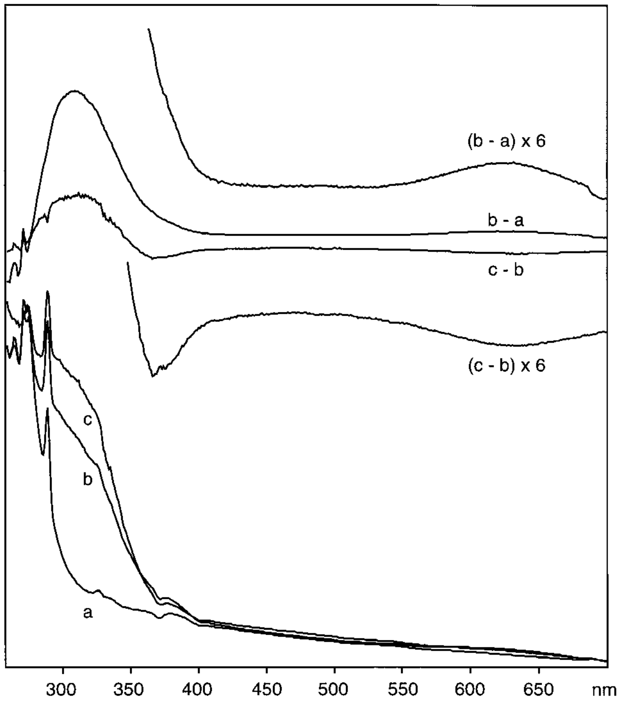
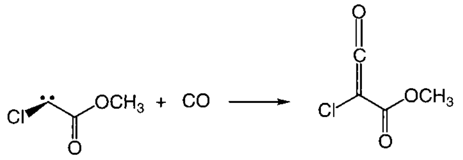


Figure 2. UV/vis spectra in an Ar matrix: (a) before the photolysis of **5**; (b) after 254 nm photolysis for 11 min; (c) after subsequent 350 nm for 10 min. The corresponding difference spectra are shown at the top.

Photolysis of **5** in argon containing 4.5% CO again produces carbene **6**, but in reduced yield. The experimental spectra in the presence and absence of CO are very similar, but two new bands at 1320 and 2144 cm^{-1} are observed only in the presence of CO (cf. Figure S1 in Supporting Information). These two bands are in good agreement with prominent vibrational transitions of ketene **9** predicted at 1320 and 2167 cm^{-1} by B3LYP/6-31G* (after scaling by a factor of 0.97). This demonstrates that a CO trappable species (e.g. carbene **6**) is produced upon photolysis of **5**.



6 **9**

Photolysis of **6** in argon with either 350 or 650 nm light bleaches both the UV and the visible absorption bands of the carbene. This is accompanied by several changes in the IR spectra (see Figure S9, Supporting Information). From these we conclude that one significant reaction of excited **6** appears to be retro-cycloaddition to indane (which is trapped in the same matrix cavity as **6**) to re-form the starting material, **5**. Photolysis of **6** also appears to induce WR to form a small amount of ketene **10** (experiment, 2148 cm^{-1}; calculation, 2167 cm^{-1}; see Supporting Information) as well as cyclization to a β-lactone, a process that has precedent.[13,17,19] The observed carbonyl frequency of the β-lactone **11** that arises by cyclization of **6** (1854 cm^{-1}) is in satisfactory agreement with the calculated value (1899 cm^{-1}). A second species is observed (1877 cm^{-1}) that may also be a β-lactone, but is currently unidentified.

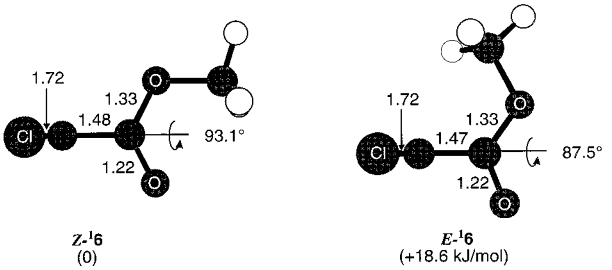


Figure 3. The B3LYP/6-31G* equilibrium geometries and relative energies (in parentheses) of the two conformers of ^{1}**6**.

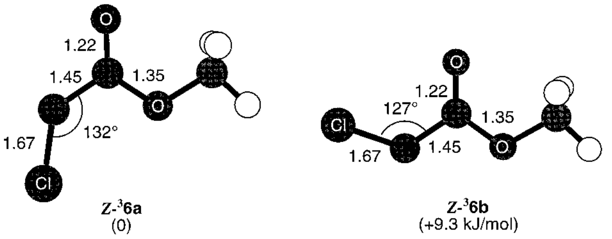


Figure 4. The B3LYP/6-31G* equilibrium geometries and relative energies (in parentheses) of the two most stable conformers of ^{3}**6** (conformer *Z*-^{3}**6a** is 9.6 kJ/mol lower in energy than *Z*-^{1}**6**).

Finally, **6** appears to lose a small amount of carbon monoxide (2139 cm^{-1}) upon photolysis. Some carbon monoxide is always produced upon 254 nm photolysis of precursor **5**.

II.3. Density Functional Calculations. B3LYP density functional calculations[20,21] were performed with the 6-31G* basis set to interpret the above spectroscopic results. The geometries of various conformers of the singlet and triplet state of carbene **6** were fully optimized, and the minima were identified by harmonic vibrational frequency calculations. More extensive calculations on **6** are reported by Scott et al.[8]

As in the case of other carbonyl carbenes, the singlet state of carbomethoxychlorocarbene (^{1}**6**) was found to be nonplanar.[5-8] Two stable conformations of ^{1}**6** were found (Figure 3) whereby the *Z*-conformation is 18.6 kJ/mol lower in energy than the *E*-conformation as is typical for *Z*- and *E*-conformations of esters.[22] A transition structure connecting *Z*- and *E*-conformations was found to lie 46.2 kJ/mol above the anti isomer.

The triplet carbene (^{3}**6**) was optimized within C_s symmetry. Four planar conformations were found, two of which (*Z*-^{3}**6a** and *Z*-^{3}**6b**) are depicted at the bottom of Figure 4 (the other two (which are not shown) represent the higher lying *E*-conformers *E*-^{3}**6c** and *E*-^{3}**6d**). The most stable structure of the triplet carbene, ^{3}**6a**, is found to be 9.3 kJ/mol more stable than the lowest energy conformation of the singlet carbene by B3LYP/6-31G*. However, this theoretical model predicts that the triplet state of methylene is stabilized by 55.2 kJ/mol relative to its lowest energy singlet state[8] which is 17.5 kcal/mol more than is found experimentally. On the other hand, the G3(MP2) method which successfully reproduces the singlet−triplet splitting of methylene (calculated, 39.5 kJ/mol;[8] experiment, 37.7

---

[19] Richardson, D. C.; Hendrick, M. E.; Jones, M., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 3790.

[20] (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[21] (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Labanowski, J. W.; Andzelm, J. *Density Functional Methods in Chemistry*; Springer: New York, 1991. (c) Parr, R. G.; Yang, W. *Density Functional Theory in Atoms and Molecules*; Oxford University Press: New York, 1989.

[22] In each case, the calculation was performed for the Z-conformation about the CO−OCH$_3$ bond. Experiments (Blom, C. E.; Günthard, Hs. H. *Chem. Phys. Lett.* **1981**, *84*, 267) and calculations (Wang, X.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 1870−1872. Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 1872−1874) likewise show that the Z-conformations of esters are more stable than the E-conformations by 5−10 kcal/mol, due to unfavorable dipolar interactions in the latter.

Table 1. B3LYP/6-31G* Harmonic Frequencies of Singlet *E*- and ***Z*-6**[a] and the Experimental IR Spectrum of **6** Observed in an Argon Matrix

	calcd for ***Z*-6**		calcd for ***E*-6**		
mode	cm^{-1}	I^b	cm^{-1}	I^b	obsd
1	76	0.5	88	0.15	
2	95	0.1	100	0.17	
3	118	0.6	157	1.3	
4	237	0.3	211	7.2	
5	245	2.3	233	3.9	
6	311	15.5	349	9.7	
7	536	4.4	520	3.5	
8	732	18.1	652	14.2	737 (w)
9	777	14.3	763	4.7	757 (w)
10	861	9.2	857	43.1	883 (w)
11	1001	33.4	1045	22.7	1007 (m)
12	1144	0.3	1143	0.65	
13	1180	3.9	1156	3.0	
14	1297	100	1311	100	1270 (vs)
15	1445	3.3	1456	4.1	1437 (vw)
16	1468	2.2	1473	5.9	1462 (vw)
17	1476	2.3	1481	4.5	1485 (vw)
18	1702	57.9	1706	79.1	1702 (s)
19	2991	6.1	2968	3.9	2997 (vw)
20	3069	4.1	3042	5.4	3029 (vw)
21	3101	2.8	3090	3.3	

[a] All calculated frequencies are scaled by a factor of 0.97. [b] Intensities relative to the strongest transition at 1297 cm^{-1} (*Z*-**6**) or 1311 cm^{-1} (*E*-**6**).

Table 2. Excited States of Singlet Carbomethoxychlorocarbene *Z*-**6** from TD-B3LYP/6-31G* Calculations

excited state	λ (nm)	*f*	excitations[a]	coefficient[b]
1	648	0.0001	27 → 28	0.51383
2	290	0.0026	26 → 28	0.59061
			27 → 29	0.25220
3	277	0.0001	25 → 28	0.69244
4	249	0.0093	24 → 28	0.10695
			26 → 28	−0.17986
			26 → 29	−0.14777
			27 → 29	0.56320

[a] In terms of molecular orbitals some of which are depicted in Figure 5. [b] Contribution of excited configuration $x \rightarrow y$ to the excited-state wave function.

kJ/mol[23]) predicts that the singlet state of **6** is 16.0 kJ/mol more stable than its triplet state.[8]

The harmonic frequencies for the *Z*- and *E*-conformers of singlet carbene **6** computed by B3LYP/6-31G* are given in Table 1 along with the experimentally observed values. Vibrational frequencies for the lowest energy conformer of triplet carbene (^{3}**6a**) are listed in the Supporting Information. The experimental IR spectrum of carbene **6** (Figure 1) is clearly more consistent with the calculated vibrational spectrum of the singlet, rather than the triplet state of the carbene.

The very strong band at 1702 cm^{-1} is attributed to the carbonyl stretch of singlet **6**. This compares to carbonyl stretching frequencies of 1660 and 1625 cm^{-1} for naphthylcarbene esters **4T** and **4S**, respectively.[13] The IR bands at 1270 and 1007 cm^{-1} are assigned to C−O single bond stretches of singlet carbene **6**. Thus, although B3-LYP/6-31G* fails to correctly predict the ground state of **6** it adequately simulates the experimental IR spectrum of singlet carbomethoxychlorocarbene.

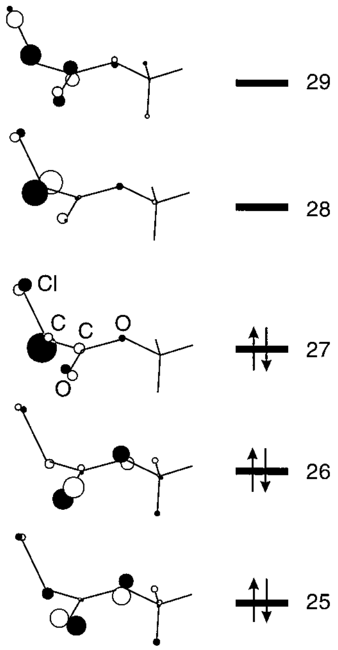
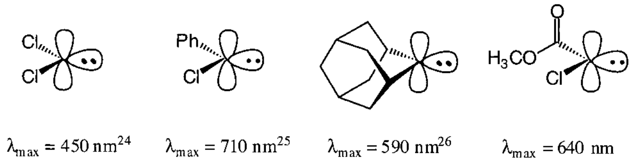


Figure 5. The molecular orbitals involved in the electronic transitions of carbomethoxychlorocarbene listed in Table 2.

Singlet carbenes typically have characteristic broad absorption bands in the visible region associated with the promotion of an electron from the HOMO (in-plane σ orbital) to the LUMO (out-of-plane pure p orbital).[24−26] The absorption maxima of this transition for a few carbenes are shown below. Thus, we assign the absorption of **6** at 640 nm to promotion of an electron from the HOMO to the LUMO of the carbene.



This assignment is validated by TD-B3LYP/6-31G* calculations on *Z*-**6** (see Table 2). This method predicts a transition with a very small oscillator strength at 648 nm that is due to promotion of an electron from the σ HOMO to the π LUMO. It also predicts two intense transitions at 249 and 289 nm which we cannot clearly resolve in the experimental spectra. However, it is tempting to associate the predicted transition at 289 nm with the band observed at 320 nm in argon. The orbitals involved in these transitions are shown in Figure 5.

The TD-B3LYP/6-31G* method was also applied to the lowest energy conformer of the triplet of **6**, and it predicts that the three lowest energy transitions are at 303, 339, and 377 nm with oscillator strengths of 0.0001, 0.0230, and 0.0004, respectively (full details can be found in the Supporting Information). The calculated electronic spectrum of singlet **6**, especially the diagnostic HOMO-LUMO transition in the visible region, is more consistent with the experimental spectrum than the calculated spectrum of the triplet carbene.

II.4. Chemical Trapping of Carbomethoxychlorocarbene. When precursor **5** was dissolved in Freon-113 ($CF_2ClCFCl_2$) and exposed to 300 nm radiation (Quartz, Ray-O-Net), indane was formed in 97% absolute yield (GC, decane as internal

---

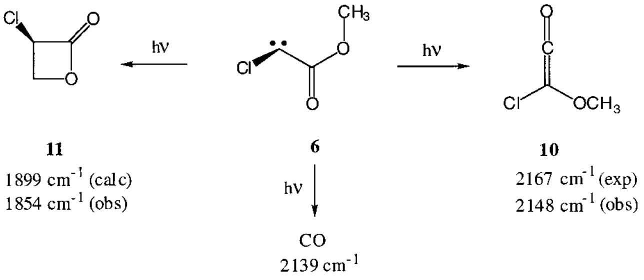
[23] Leopold, D. G.; Murray, K. K.; Stevens-Miller, A. E.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849.

[24] Milligan, D. E.; Jacob, M. E. *J. Chem. Phys.* **1967**, *47*, 703.

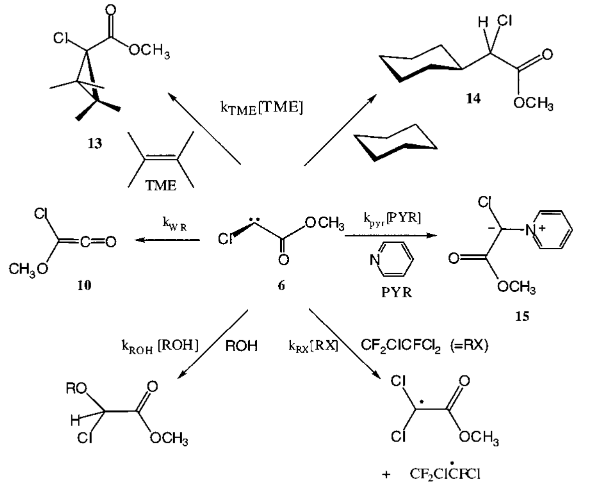
[25] Pliego, J. R., Jr.; De Almedia, W. B.; Celebi, S.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A* **1995**, *103*, 7481.

[26] Bally, T.; Matzinger, S.; Truttmann, L.; Platz, M. S.; Morgan, S. *Angew Chem., Int. Ed. Engl.* **1994**, *33*, 19.

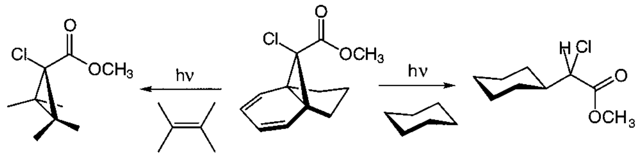
Scheme 1



Scheme 2



standard). Similarly, photolysis in neat cyclohexane or 2,3-dimethyl-2-butene (tetramethylethylene, TME), respectively, led to the clean formation of indane and a carbene-solvent adduct.



13 **5** **14**

Adducts **13** and **14** were formed in 85% and 16% yield, respectively, relative to indane, as demonstrated by NMR spectroscopy. Thus, there is little doubt that carbene **6** is formed from **5** in solution. Although LFP studies (vide infra) suggest that Freon-113 is not an inert solvent, conclusive evidence for the formation of any adducts between **6** and this solvent was not obtained by GC-MS analysis. The most likely mode of carbene reaction with Freon-113 is chlorine atom abstraction to form a radical pair,[15] as shown in Scheme 2.

The yield of cyclopropane adduct **13** was measured as a function of the concentration of TME in Freon-113. As expected, the yield increases initially upon increasing [TME] and then attains a limiting value. Plotting one over the yield of **13** versus 1/[TME] gives a straight line from which we can obtain $k_{\mathrm{TME}}\cdot\tau$, where τ (=$1/k_{\mathrm{OBS}}$) is the lifetime of carbene **6** in Freon-113 in the absence of TME. A plot of $\ln(k_{\mathrm{TME}}/k_{\mathrm{OBS}})$ versus $1/T$ between 223 and 303 K is also linear and it yields $E_a^{\mathrm{TME}} - E_a^0 = 3.0$ kJ/mol and $A^{\mathrm{TME}}/A^0 = 2.2$, where the superscripts refer to the Arrhenius parameters for carbene reaction with TME, and the decay of the carbene in Freon-113 in the absence of TME by all processes, such as Wolff rearrangement and reaction with solvent, which consume the carbene in the absence of TME.

Table 3. Values of $k_{\mathrm{pyr}}\tau$ Obtained in Various Solvents at Ambient Temperature

solvent	$k_{\mathrm{pyr}}\tau$	τ [ns][a]
acetonitrile	1.4 ± 0.4	0.7
acetonitrile-d_3	3.5 ± 0.3	2
cyclopropyl cyanide	11 ± 2	6
pentane	89 ± 12	45
benzene	32 ± 2	16
cyclohexane	36 ± 6	18
cyclohexane-d_{12}	93 ± 7.4	47

[a] Assuming $k_{\mathrm{pyr}} = 2 \times 10^9$ M^{-1} s^{-1} as in Freon-113.

II.5. Laser Flash Photolysis (LFP) Studies. LFP of **5** in Freon-113 at ambient temperature fails to produce a useful transient. The broad absorption of **6** detected in argon at 14 K at 640 nm is too weak to be of value in LFP experiments. However, LFP of **5** in pentane containing 1.03 M pyridine produces a transient spectrum with an intense, broad band peaking at 440 nm (Figure S2 in the Supporting Information), which is attributed to ylide **15** (Scheme 2).

It was possible to follow the formation of **15** in Freon-113 (Figure S3, Supporting Information) and in perfluorohexane. The ylide was formed in an exponential process that could be analyzed to yield k_{obs}, the observed rate constant of ylide formation. As expected for a carbene with a singlet ground state, the magnitude of k_{obs} was not sensitive to the presence of oxygen.

According to Scheme 2, k_{obs} can be equated to various elementary rate constants as shown in eq 1, where k_{WR}, k_{RX},

$$k_{\mathrm{obs}} = k_{\mathrm{WR}} + k_{\mathrm{RX}}[\mathrm{RX}] + k_{\mathrm{pyr}}[\mathrm{PYR}] \qquad (1)$$

and k_{pyr} are as defined in Scheme 2, while [RX] and [PYR] denote the concentrations of the Freon and pyridine, respectively.

A plot of k_{obs} versus [PYR] in Freon-113 is linear (Figure S5 in the Supporting Information) with a slope that corresponds to $k_{\mathrm{pyr}} = 2.0 \times 10^9$ M^{-1} s^{-1} at ambient temperature. This is comparable to other carbene rate constants with pyridine.[17] The intercept of this plot is $k_{\mathrm{WR}} + k_{\mathrm{RX}}[\mathrm{RX}]$, which is $1/\tau$, where τ is the carbene lifetime under these conditions (114 ns). These experiments were repeated in perfluorohexane, in which the carbene has a lifetime of 354 ns at ambient temperature.

In other, more reactive solvents, the yield of ylide was measured as a function of pyridine concentration by transient optical spectroscopy. A double reciprocal treatment of the data is linear, as shown in the insert to Figure S5 of the Supporting Information. The ratio of the intercept and the slope of such a plot is $k_{\mathrm{pyr}}\cdot\tau$. These data are collected in Table 3 and analyzed using the k_{pyr} value measured in Freon-113, assuming that k_{pyr} is independent of solvent. In this manner it is found that the lifetime of **6** in cyclohexane is 2.6 times shorter than that in cyclohexane-d_{12}. This is consistent with our previously discussed product study which demonstrates that the lifetime of **6** in cyclohexane is controlled to some extent by insertion into a C−H bond of the solvent. The lifetimes of **6** in benzene and in acetonitrile are both comparatively short. This could be due to a solvent effect on either k_{pyr} or k_{WR} or more likely due to rapid chemical reaction of the carbene with the solvent.

The yield of **15** in Freon-113 containing a constant concentration [PYR] = 0.01M is diminished by the presence of a competitive carbene quencher such as ethanol (EtOH) or 2,3-dimethyl-2-butene (DMB). Stern−Volmer treatment of the data (cf. Figure S6 in the Supporting Information) reveals that $k_{\mathrm{EtOH}}/k_{\mathrm{pyr}}$ is 35 and $k_{\mathrm{TME}}/k_{\mathrm{pyr}}$ is 23.3. As $k_{\mathrm{pyr}} = 2 \times 10^9$ M^{-1} s^{-1} then $k_{\mathrm{EtOH}} = 7.0 \times 10^8$ M^{-1} s^{-1} and $k_{\mathrm{DMB}} = 4.1 \times 10^8$ M^{-1} s^{-1} in Freon-113.

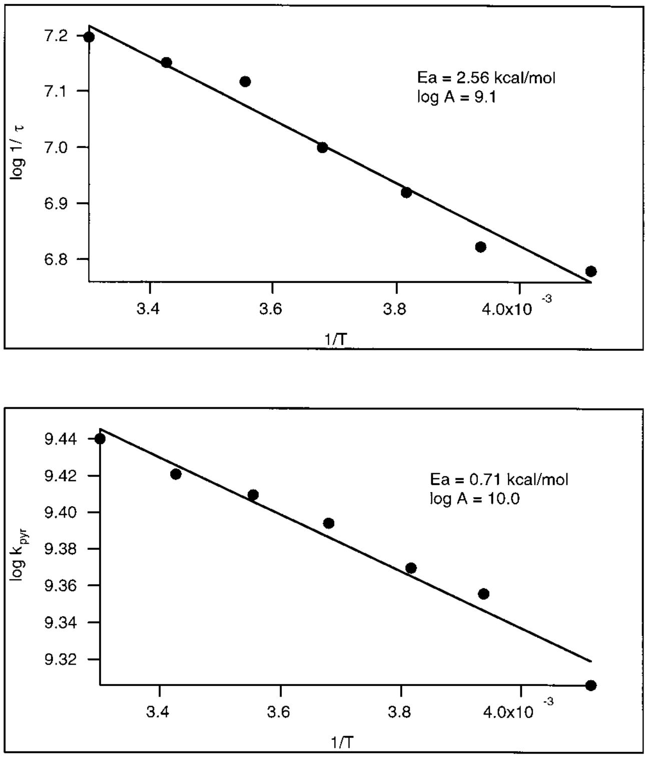


Figure 6. Arrhenius treatment of the k_{PYR} and $1/\tau$ data of carbomethoxychlorocarbene in Freon-113 (top) and Arrhenius treatment of the k_{PYR} and $1/\tau$ data (bottom).

We also studied the temperature dependence of the observed rate constant for the formation of ylide **13** in Freon-113 as a function of the pyridine. Arrhenius treatment of $k_{pyr}(T)$ reveals that $E_a = 10.9 \pm 0.8$ kJ/mol and $A = 10^{9.1\pm0.2}$ s^{-1} for the carbene disappearance in Freon-113 between 243 and 303 K. These data can be combined with those from the TME trapping study to deduce $E_a^{TME} = 13.8$ kJ/mol and $A^{TME} = 10^{11.3}$ s^{-1} which appear reasonable in comparison with the same parameters measured for other carbenes.[17] A plot of $\ln(1/\tau)$ and $\ln k_{PYR}$ versus $1/T$ in perfluorohexane is shown in Figure 6, which yields a barrier to carbene disappearance of 23.4 ± 1.7 kJ/mol and $A = 10^{10.6\pm0.3}$ s^{-1} in this solvent.

III. Discussion

Calculations indicate that methylene, formylcarbene, and carbomethoxycarbene have triplet ground states.[5−8] Triplet ground state multiplicities have been established experimentally for methylene[23] and carbomethoxycarbene.[10] The ground-state multiplicity of formylcarbene has not yet been demonstrated spectroscopically.[9]

B3LYP/6-31G* calculations consistently predict triplet states of carbenes which are too stable relative to their corresponding singlet states.[8] In contrast, the G3(MP2) model successfully reproduces ST splittings in carbenes where these values have been experimentally determined.[8] This computational method predicts that singlet carbomethoxychlorocarbene (**6**) is 16.0 kJ/mol more stable than the lowest energy triplet species. This is consistent with the matrix IR and UV−vis spectra of **6**, as well as the low rate constant for its reaction with oxygen in solution. Thus, **6** is the first ground-state singlet carbonylcarbene to be studied by fast kinetic methods and, unlike ground-state triplet carbenes, its kinetics can be analyzed without concerns related to issues of spin interconversion.

Formylcarbene and carbomethoxycarbene have been studied previously by transient spectroscopy using the pyridine ylide method.[2,3] The lifetimes of both carbenes were found to be ≈1 ns in solution at ambient temperature and they were comparable in cyclohexane and cyclohexane-d_{12} which indicated that the carbene lifetimes are controlled by intramolecular Wolff rearrangement rather than by reaction with solvent. It seems likely that spin state equilibration of formyl and carbomethoxycarbene is complete within 1 ns, based on analogy to arylcarbenes.[27] Because the lifetimes of these carbenes were shorter than the time resolution of the spectrometer, only the ratio of k_{WR}/k_{PYR} could be determined. This ratio showed little variation with temperature. In the present work, the *absolute* value of the activation energy of the reaction of **6** with pyridine could be measured directly and it was found to be 2.9, 4.2, and 5.9 kJ/mol in Freon-113, perfluorohexane and α,α,α-trifluorotoluene, respectively. Thus, the barrier to WR of formyl and carbomethoxy carbene in solution must lie between 0 and 10 kJ/mol.[17] This value is smaller than that predicted (G3(MP2), 0 K) by Scott et al. for the gas-phase Wolff rearrangement of formylcarbene (24.9 kJ/mol) and carbomethoxycarbene (25.7 kJ/mol).[8,28] The best theoretical estimate of the gas-phase barrier for formylcarbene using the W1′ method is 18.5 kJ/mol.[8] According to SCI-PCM calculations the barrier for formylcarbene is reduced in solution by 2 (dielectric constant = 2) to 6 (dielectric constant =40) kJ/mol in solution thus bringing the predicted barriers into closer agreement with those estimated in solution by the LFP experiments.

The experimental barrier to disappearance of spin-equilibrated carbomethoxy-2-naphthylcarbene in Freon-113 (presumably by Wolff rearrangement) is 14.2 kJ/mol.[15] As the singlet−triplet splitting of this carbene is only 0.8 kJ/mol in this solvent, nearly all of this barrier must be on the singlet surface between carbene and ketene.

The activation barriers for the disappearance of carbomethoxychlorocarbene (**6**) are 5.4, 10.9, and 24.7 kJ/mol in α,α,α-trifluorotoluene, Freon-113, and perfluorohexane, respectively. The barrier is largest in perfluorohexane, the most inert solvent. In all three solvents the experimental barrier for carbene disappearance is much lower than that predicted (58.2 kJ/mol) for isolated **6** at the G3(MP2) level, and it is unlikely that higher level calculations or the consideration of solvent polarity will substantially improve the agreement between theory and this experimental result. The small barriers in α,α,α-trifluorotoluene and Freon-113 are readily explained by reaction between the carbene and the solvent.

Surely the fraction of **6** decaying by Wolff rearrangement in perfluorohexane is greater than that in α,α,α-trifluorotoluene and Freon-113, hence the larger barrier, but we cannot prove that it is the sole process consuming this carbene under our experimental conditions. It is not likely that carbene **6** will abstract a fluorine atom from perfluorohexane**.** However, **5** is only sparingly soluble in perfluorohexane and one can speculate that the precursor is not homogeneously dispersed in this solvent, so that photogenerated carbene **6** is born in an environment enriched in precursor, and that part of its decay proceeds by reaction with precursor. Thus, we can only state with confidence that the lower limit of the barrier to Wolff rearrangement of carbomethoxychlorocarbene is ≥24.7 kJ/mol.

IV. Conclusions

Methyl 8-chloro-3a,7a-methanoindan-8-carboxylate (**5**) was deposited in an argon matrix at 14 K. Photolysis (254 nm) of

---

(27) (a) Sitzman, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868. (b) Grasse, P. B.; Braver, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.

(28) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

this substance led to its disappearance and the formation of carbomethoxychlorocarbene (**6**). B3LYP/6-31G* calculations reveal that there are only two conformations of the nonplanar singlet (i.e. the *E*- and *Z*-conformations of the carboxylate group), whereas four conformations of the planar triplet carbene are found. The matrix IR spectrum is consistent with the presence of a mixture of singlet carbene conformations with a carbonyl stretch at 1702 cm^{-1} and prominent bands at 1270, 1007, and 757 cm^{-1}. Indane may contibute to the last band. There is a broad weak band in the visible at 640 nm corresponding to electron promotion from the HOMO to the LUMO of the carbene. Photolysis (300 nm) of the precursor in solution generates indane and carbomethoxychlorocarbene which can be intercepted with cyclohexane or 2,3-dimethyl-2-butene. Laser flash photolysis of the precursor in Freon-113 ($CF_2ClCFCl_2$) or perfluorohexane produces carbomethoxychlorocarbene, which can be trapped with pyridine to form an ylide. It was possible to measure the growth of the ylide as a function of pyridine concentration. Analysis of the data indicates that the carbene lifetime is 114 ns in Freon-113 at ambient temperature and decays with $E_a = 11.1$ kJ/mol and $A = 10^{9.1}\ \text{s}^{-1}$. This analysis was repeated in perfluorohexane to yield Arrhenius parameters $E_a = 24.7 \pm 1.7$ kJ/mol and $A = 10^{10.6\pm0.3}\ \text{s}^{-1}$ ($\tau = 354$ ns at 293 K). The activation barrier determined in perfluorohexane is the lower limit of the barrier to Wolff rearrangement of carbomethoxychlorocarbene.

V. Experimental Section

General Methods. ^{1}H NMR spectra were obtained on a Bruker DRX-500 (500 MHz) spectrometer. IR spectra were recorded on a Perkin-Elmer 1710 Fourier transform spectrometer interfaced with a Perkin-Elmer 3700 data station. The GC-MS spectrometer was an HP-6890 Series GC System with an HP-1 methyl siloxane capillary column (40.0 m × 100 μm × 0.20 μm). The gas chromatograph was linked to an HP 5973 mass selective detector.

Tetrahydrofuran, diethyl ether, benzene, and cyclohexane were purified by distillation from sodium−benzophenone and stored under an argon atmosphere. Freon-113, perfluorohexane, ethanol, cyclohexane-d_{12}, acetonitrile, and pentane were purchased from Aldrich Chemical Co. 2,3-Dimethyl-2-butene was dried by passing through a plug of neutral alumina prior to use. The absolute yields of adducts **13** and **14** were obtained by ^{1}H NMR integration using indane (which is derived from precursor **5**) as an internal standard.

Laser Flash Photolysis Studies.[29] For LFP studies of precursor **5**, a stock solution in Freon-113 or perfluorohexane was prepared with an optical density of 0.1−0.3 and placed in a 3 mL cuvette. The LFP apparatus utilized a Lambda Physik LPX-100 excimer laser (308 nm, 120 mL, 10 ns). LFP experiments required samples to be deoxygenated by passing a flow of argon through the sample for 2 min. The analysis of the data was performed with the program *Igor Pro* by Wavemetrics. Transient absorption spectra were obtained on an EG&G PARC 1460 optical multichannel analyzer fitted with an EG&G PARC 1304 pulse amplifier, EG&G PARC 1024 UV detector, and a Jarrell-Ash 1234 grating. Low-temperature LFP experiments were performed using an NESLAB RTE-110 proportional temperature controller to regulate the temperature.

10-*exo*-Carbomethoxy-10-chlorotricyclo[4.3.1.0^{1,6}]decadiene-2,4 (5). To a stirred solution of 10,10′-dichlorotricyclo[4.3.1.0^{1,6}]-decadiene-2,4 [18](130 mg, 0.65 mmol) in 4 mL of THF freshly distilled from sodium benzophenone ketyl cooled to −78 °C was added 1.6 M *n*-butyllithium solution in hexanes (0.42 mL) dropwise under argon. The dark blue mixture was stirred at −78 °C for 2 h, then poured over crushed dry ice, allowed to warm to room temperature, and evaporated with a rotary evaporator. The solid lithium salt thus obtained was washed with ice cold ether (1 mL) dissolved in DMSO (1.5 mL) and then iodomethane (0.05 mL, 0.8 mmol) was added. The mixture was stirred for 0.5 h at room temperature, poured into ice water (15 mL), extracted with ether (4 × 10 mL), washed with water and brine, dried over sodium sulfate, decolorized with charcoal, filtered, and evaporated. The yield was 110 mg (75.7%)of white solid, mp 67−69 °C (2-propanol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.11−6.19 (m, 2H), 5.86−5.95 (m, 2H), 3.83 (s, 3H), 2.42−2.55 (m, 2H), 1.86−2.03 (m, 2H), 1.57−1.70 (m, 1H), 0.86−1.00 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 168.14, 124.27, 122.98, 53.06, 45.15, 33.18, 29.66, 19.92; HRMS calcd for $C_{12}H_{13}Cl^{35}O_2$ 224.0604, found 224.0604.

Adduct 13. Precursor **5** (100 mg) in neat 2,3-dimethyl-2-butene was irradiated (300 nm) for 16 h after bubbling with dry argon for several minutes. The remaining 2,3-dimethyl-2-butene was removed by rotary evaporation and the mixture was chromatographed (silica, 5% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 3.68 (s, 3H), 1.14 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 169.1, 55.7, 52.8, 29.3, 19.5, 19.4; IR 1736.7 cm^{-1}; MS(EI) *m/z* (rel intensity) 191(M, 1), 175 (100), 143 (35), 123 (41), 95 (55), 73 (84); HRMS(EI) calcd for $C_9Cl^{35}H_{15}O_2$ (M) 190.0761, found 190.0792.

Adduct 14. Precursor **5** (200 mg) in neat cyclohexane was irradiated (300 nm) for 16 h after bubbling with dry argon for several minutes. The remaining cyclohexane was removed by rotary evaporation and the mixture was chromatographed (silica, 5% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 4.02 (d, 1H, $J = 7.0$ Hz), 3.71 (s, 3H), 1.86 (m, 2H), 1.70 (m, 2H), 1.59 (m, 2H), 1.19 (m, 2H), 1.07 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 170.4, 63.4, 53.1, 42.2, 30.3, 29.1, 26.3, 26.1, 26.0; MS(EI) *m/z* (rel intensity) 191 (M, 1), 155 (2), 131 (3), 108 (100), 55 (29); HRMS(EI) calcd for $C_9Cl^{35}H_{15}O_2$ (M) 190.0761, found 190.0717.

Matrix Isolation Spectroscopy. The precursor was put in a glass U tube that was directly connected to a helium closed cycle cryostat (Air Products). Argon gas streaming over the precursor was condensed on the surface of a CsI window held at ca. 20 K. Once formed, the argon matrix was maintained at 14 K during the entire experiment. UV−vis spectra were measured with a Perkin-Elmer Lambda 6 UV−vis spectrophotometer and the IR spectra were recorded on an Perkin-Elmer FT-IR 2000 interfrerometer at 0.2 cm^{-1}. Ray-O-Net lamps were used to photolyze the sample and IR and UV−vis spectra were recorded after each step of the photolysis cycle.

Density Functional Calculations. Geometries of singlet and triplet chlorocarbomethoxy carbene were fully optimized at the B3LYP level using the 6-31G* basis set and harmonic frequencies were calculated at the same level. Four triplet and two singlet carbene conformers were identified. A transition state structure connecting the two singlet conformers was found. C_s symmetry was maintained during the optimizations for the triplet states. As higher level calculations predict the singlet to be the ground state of **6**,[8] the calculated frequencies of the singlet carbenes were employed in the analysis of IR spectra. All calculations were carried out with the Gaussian 94 and Gaussian 98 program packages.[30]

---

(29) Gristan, N. P.; Zhai, H. B.; Yuzawa, T.; Karweik, D.; Brooke, J.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 2833.

(30) (a) 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., Jr.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Avala, 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. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.3;Gaussian, Inc.: Pittsburgh, PA, 1995. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Cliford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stafanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Goperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.6; Gaussian, Inc.: Pittsburgh, PA 1998.

Acknowledgment. Support of this work by the NSF is gratefully acknowledged (CHE-9613861). The authors are indebted to Professors Berson and Wiberg of Yale University for their generous donation of the matrix isolation equipment used in this work. The authors gratefully acknowledge a critical reading of this manuscript by Professor Thomas Bally.

Supporting Information Available: Experimental data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA004235M