

Carbomethoxyfluorocarbene

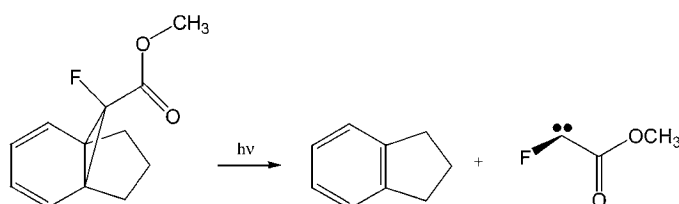
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ABSTRACT



Carbomethoxyfluorocarbene was studied in solution by laser flash photolysis with UV–vis and infrared detection. In contrast to expectations, carbomethoxyfluorocarbene is more reactive than carbomethoxychlorocarbene.

Theory predicts that halogen substituents will dramatically modify the absolute reactivity of carbene esters.¹ To date, only one member of this class of compounds, carbomethoxychlorocarbene, has been studied by chemical and physical methods.² Herein, we report the extension of this work to carbomethoxyfluorocarbene **1**.

Fluorochlorodiene **2**, as a mixture of endo–exo isomers,³ was metalated by treatment with *n*-butyllithium in THF at -78°C (Scheme 1). The organolithium reagent was reacted with crushed carbon dioxide to form a carboxylate salt which

was methylated with iodomethane in DMSO to give **3** in 75% yield.

The structure of **3** was confirmed by X-ray crystallography (see the Supporting Information).

Photolysis (300 nm) of **3** in neat tetramethylethylene (TME) leads to consumption of precursor and formation of indan and cyclopropane **4** in 98 and 27% yield, respectively (Scheme 1). This result demonstrates that photolysis of **3** generates carbomethoxyfluorocarbene **1** in solution.

Laser flash photolysis (LFP, 308 nm) of **3** in cyclohexane fails to produce a UV–vis active transient. LFP in the

Scheme 1

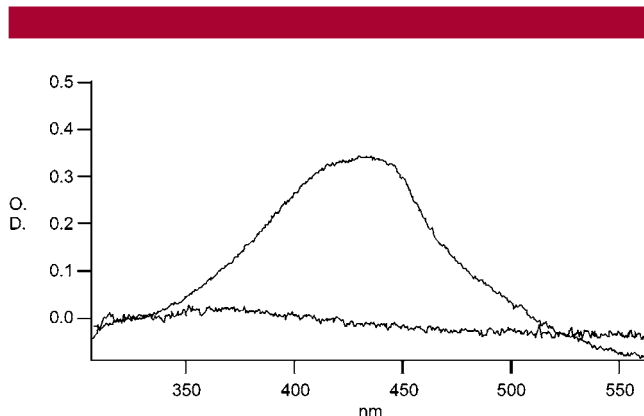
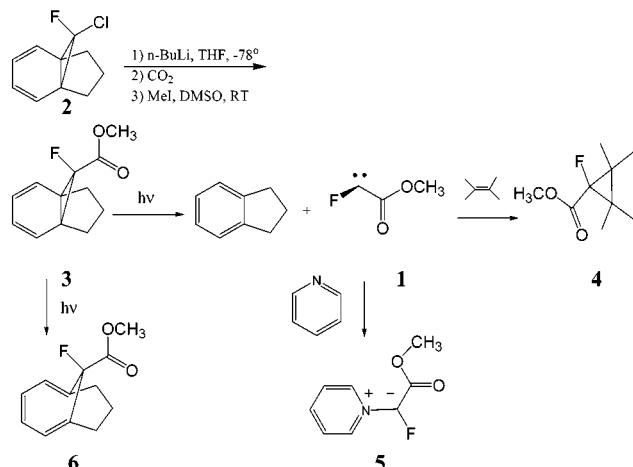


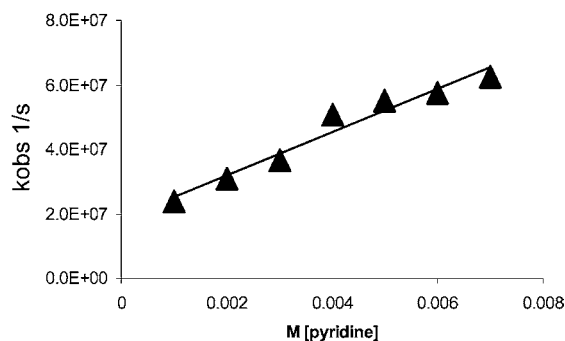
Figure 1. LFP of **3** in cyclohexane with (top) and without (bottom) 1 M pyridine.

Table 1. Values for the Absolute Rate Constant of **1** and Carbomethoxychlorocarbene with Several Quenchers

quencher	kinetic expression	carbomethoxyfluorocarbene	carbomethoxychlorocarbene ^a
		$k_{\text{quencher}} (\text{M}^{-1} \text{s}^{-1})$	$k_{\text{quencher}} (\text{M}^{-1} \text{s}^{-1})$
pyridine	k_{obs} vs [pyridine]	6.7×10^9	2.0×10^9
methanol	Stern–Volmer ^b	1.2×10^9	7.0×10^8 ^c
TME	Stern–Volmer ^b	1.1×10^9	4.1×10^8
THF	Stern–Volmer ^b	2.1×10^9	N/A

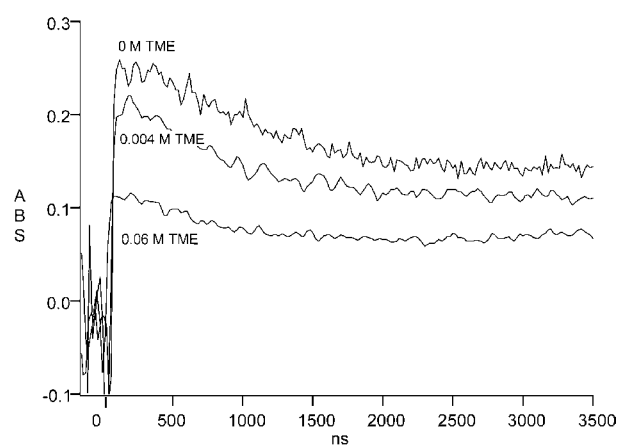
^a From ref 2. ^b 0.005 M [pyridine]. ^c Ethanol.

presence of 1 M pyridine under otherwise identical conditions produces an intensely absorbing transient (Figure 1). Similar results were obtained in $\text{CF}_2\text{ClCFCl}_2$, CH_2Cl_2 , CH_3CN , and benzene solvents. The transient is formed in an exponential process that can be analyzed to yield an observed rate constant, k_{obs} . A plot of k_{obs} versus pyridine is linear (Figure 2), which leads us to assign the carrier of transient absorption to ylide **5** (Scheme 1).

**Figure 2.** Plot of k_{obs} versus [pyridine] M in $\text{CF}_2\text{ClCFCl}_2$ at ambient temperatures.

The slope of the plot indicates that k_{pyr} (the absolute rate constant for reaction of carbene **1** with pyridine) is $6.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This is 3.2 times larger than the corresponding rate constant of reaction of carbomethoxychlorocarbene with pyridine. The intercept of Figure 2 is $1/\tau$ where τ is the lifetime (53 ns) of **1** in Freon-113 ($\text{CF}_2\text{ClCFCl}_2$) in the absence of pyridine. The lifetime of carbomethoxyfluorocarbene is about half that of carbomethoxychlorocarbene (114 ns) under the same conditions.² Calculations¹ indicate that the barrier to Wolff rearrangement of the fluoro and chloroesters are significant (16.9 and 13.9 kcal/mol, respectively); thus, the lifetimes are most likely controlled by bimolecular reactions of the carbenes. The yield of pyridine ylide **5** (constant [pyridine] = 0.005 M) is reduced when LFP experiments are repeated in the presence of a competitive trap of carbene **1** (e.g., TME, see Figure 3). Stern–

Volmer treatment of the data yields linear plots (Figure S2, Supporting Information). The slopes of these plots are equal to $k_{\text{Q}}/(1/\tau + k_{\text{pyr}}[\text{pyr}])$ which allows deduction of various values of k_{Q} (Table 1).

**Figure 3.** Quenching of the yield of ylide **5** in $\text{CF}_2\text{ClCFCl}_2$ by TME at constant [pyridine] = 0.005 M.

Diene **3** was deposited in argon at 18 K (Figure S3, Supporting Information). Exposure of the sample to 254 nm light for 1 h leads to the disappearance of IR bands of **3** and to the formation of two new carbonyl absorptions at 1756 and 1711 cm^{-1} . Density functional theory (DFT)⁴ (B3LYP/6-31G*) has been shown to well predict the vibrational spectrum of carbomethoxychlorocarbene² and predict carbene geometries similar to that of ab initio molecular orbital theory.¹ The fluorine atom of carbene **1** is nearly orthogonal to the plane of the ester group to allow the filled hybrid orbital to conjugate with the π system of the carbonyl group.

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(2) Likhovorik, I.; Zhu, Z.; Tae, E. L.; Tippmann, E.; Hill, B.; Platz, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 6061–6068.

(3) Buron, C.; Tippmann, E. M.; Platz, M. S. *J. Phys. Chem. A*, submitted.

(4) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785. (c) 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.; Clifford, 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.; Baboul, A. G.; Stefanov, J. V.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, 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.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

DFT predicts the carbonyl vibration of **1** will be at 1712 cm^{-1} after scaling by a factor of 0.9613. Thus, the new absorption band at 1711 cm^{-1} formed upon matrix photolysis of **3** is attributed to carbomethoxyfluorocarbene **1**.

LFP of **3** in aerated heptane produces the time-resolved infrared (TRIR) spectrum of Figure 4. The negative peak

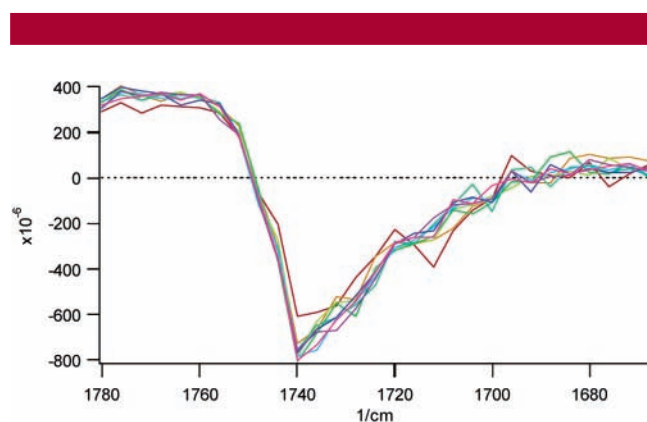


Figure 4. Time-resolved infrared spectrum for **3** in heptane. Lines follow a red to violet color progression as a function of time (1 μs elapsed per line). Positive peaks represent a new absorbance; negative peaks represent consumed species.

between 1700 and 1750 cm^{-1} is due to bleaching of **3**. The positive peak observed at 1765 cm^{-1} is formed faster than the time resolution of the spectrometer and has a lifetime in excess of 500 μs . The carrier of this band is attributed to triene **6** which is formed in a process parallel to fragmentation (Scheme 1) and is observed in an argon matrix at 1756 cm^{-1} . Similar results have been obtained with other diene precursors.⁵ Also, no new peak attributable to the Wolff rearrangement product was observed in the ketene region (2072–2160 cm^{-1}).

LFP of **3** in CD_3CN gives the transient spectrum of Figure 5 which reveals a broadly absorbing photoproduct at 1690–

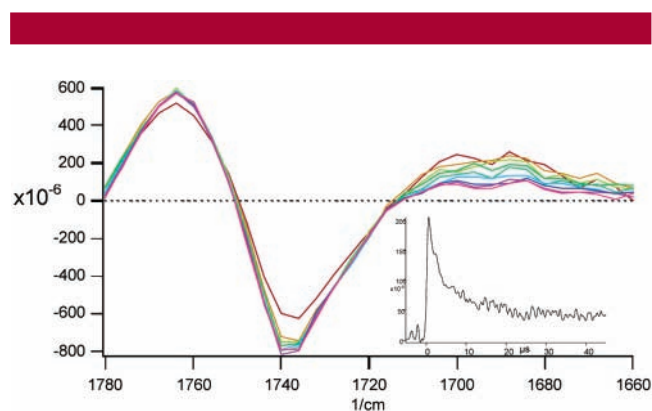
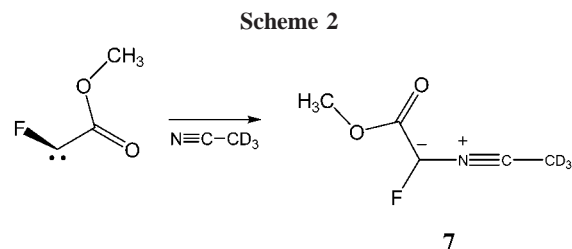


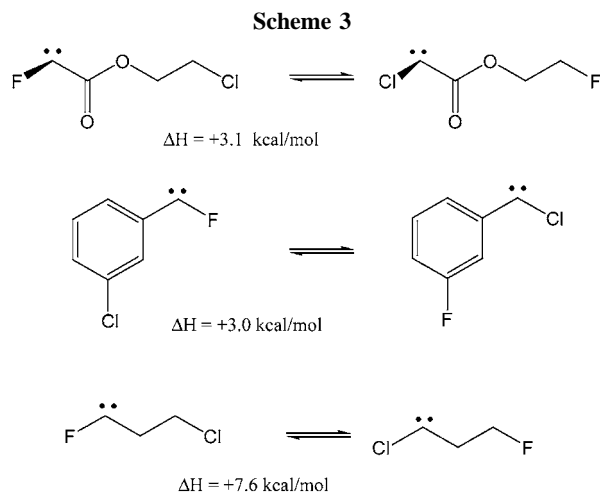
Figure 5. Time-resolved infrared spectrum for **3** in CD_3CN . Lines follow a red to violet color progression as a function of time (1 μs elapsed per line). Positive peaks represent a new absorbance; negative peaks represent consumed species. Kinetic trace recorded at 1696 cm^{-1} .

1700 cm^{-1} . The photoproduct has a lifetime of 5–12 μs and is attributed to nitrile ylide **7** (Scheme 2).



Density functional theory (B3LYP/6-31G*) predicts that nitrile ylide **7**⁶ (Scheme 2) will have a carbonyl absorption at 1717 cm^{-1} after scaling by a factor of 0.9613. Ylide **7** may well absorb at 1717 cm^{-1} , but spectral bleaching of the precursor obscures this region.

The data reveals that the fluorocarbene ester has a shorter lifetime and greater bimolecular reactivity than the chloro analogue. This is opposite to the trend observed with arylhalo carbenes.⁷ To better understand this result, DFT calculations of a series of isodesmic reactions were performed. It is clear from Scheme 3 that fluorocarbenes are thermodynamically



more stable than isomeric chlorocarbenes in the alkyl, aryl, and carboalkoxy carbene series (Supporting Information). Interestingly, it appears that the phenyl and ester groups stabilize the fluoro carbenes by ~4 kcal/mol relative to chlorocarbenes as compared to alkylhalo carbenes.

We then calculated and compared the LUMOs and performed a natural population analysis⁸ (NPA) of the fluoro-

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(6) The TRIR spectra of carbonylcarbene–nitrile ylides have been observed previously, see Wang, Y.; Hadad, C. M.; Toscano, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 1761.

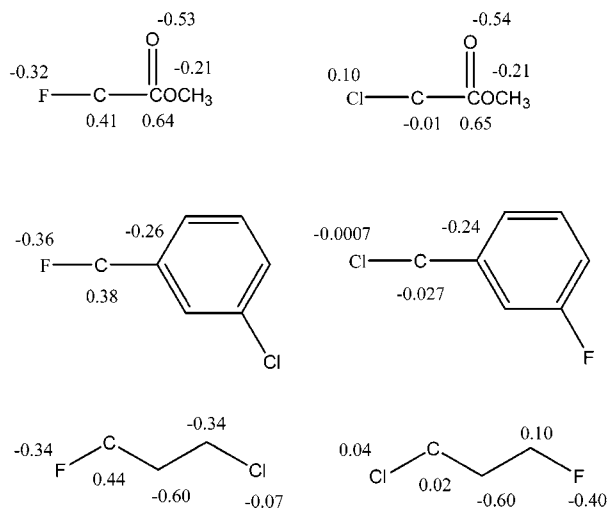
(7) Moss, R. A.; Turro, N. J. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 213.

(8) Reed, A. E.; Weinhold, F. A.; Curtiss, C. A. *Chem. Rev.* **1988**, *88*, 899.

and chlorocarbene esters. The natural population analysis indicates that the empty p orbital on the more reactive fluorocarbene ester has a lower energy and a lower population than does the chloroester carbene (Supporting Information).

Furthermore, the NPA atomic charges show that the carbenic carbon is more electrophilic in the fluoro-substituted carbenes than the chloro case (Scheme 4). In the fluoroester

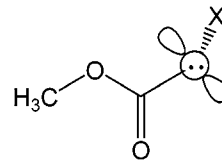
Scheme 4



carbene, effects due to the electronegativity of fluorine are larger than the effects of fluorine π back-bonding in determining reactivity. It is not yet clear why this effect is more important in determining reactivity in halocarbene esters than aryl and alkylhalocarbenes.

The explanation of the enhanced reactivity of the fluorocarbene ester may be related to its geometry. Arylhalocarbenes are planar which allows the aryl ring to stabilize the empty p orbital of the carbene. Singlet carbene esters are nonplanar (Scheme 5).¹ This allows the filled hybrid orbital

Scheme 5



of the carbene to conjugate with the π system of the carbonyl group and leaves the reactive empty p orbital of the carbene in the plane of the ester group (Scheme 5). Thus, the two substituents (aryl and ester) interact with different carbene orbitals.

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Supporting Information Available: Experimental procedures, supporting figures, and calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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