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Carboethoxycarbene. A Laser Flash Photolysis Study

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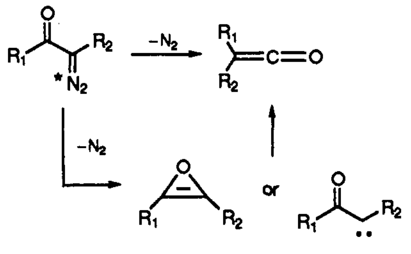
Abstract: Laser flash photolysis of ethyldiazoacetate (351 nm, 17 ns) generates carboethoxycarbene, which can be intercepted with either pyridine or acetone to produce a UV–vis active ylide. Analysis of the yield of ylide as a function of either pyridine or acetone concentration leads to estimates of the carbene lifetime. Absolute rate constants of reaction of carboethoxycarbene with alcohols, sulfides, ethers, and alkenes were deduced.

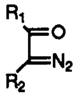
I. Introduction

Ethyl diazoacetate (EDA) is a commonly employed reagent in organic chemistry.[1] This is due, in part, to its ease of synthesis and handling. Decomposition of EDA with heat, light, or metal catalysts generates carbenes and carbenoids which can be utilized in synthetic and mechanistic studies.[2,3]

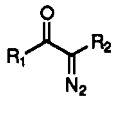
The chemistry of α-carbonyl-substituted diazo compounds and carbenes is closely associated with Wolff rearrangement (WR).[4]



Evidence has been advanced that Wolff rearrangement proceeds in the excited states of diazo precursors[5] or is mediated by an oxirene[4] or carbene[2,3] intermediate. It now seems likely that the mechanism followed is a function of R_1 and R_2 and of the conformation of the diazo precursor. Wolff rearrangement is facile in *syn* conformations of diazo precursor and is less likely in the *anti* form.[6]



syn



anti

It is clear that intermolecular carbene chemistry is much more prevalent in carbene esters than in ketocarbenes.[2,3] Carboalkoxycarbenes have been shown to add to olefins[7] and aromatics[8] and insert into the CH bonds of alkanes.[9] Unstable oxygen and halonium ylides have been proposed to explain the ultimate products of reaction of carboalkoxycarbenes and ketones,[10] ethers,[11] and halogen-containing compounds.[12] Furthermore, stable sulfur ylides have been isolated from the reaction of carboalkoxy carbenes with sulfides[13] and isoquinoline.[14] Thus, carboethoxycarbene **1** (R = Et) appeared to be an excellent candidate for study by laser flash photolysis techniques using pyridine–ylide probe methodology developed in our laboratory.[15] Herein, we are pleased to report the results of these studies. The data provide estimates of the lifetime of carboethoxycarbene, rate constants

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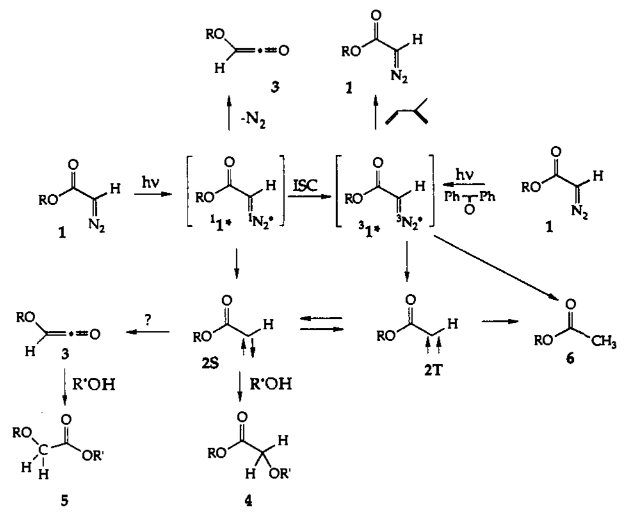
Scheme 1



for its intra- and intermolecular reactions, and insight into the mechanisms of these processes.

II. Previous Studies: Chemical Analysis of Reaction Products and Spectroscopy

The organic photochemistry of alkyl diazoacetates is well-developed and has been previously reviewed.[2,3] The mechanistic picture that emerges is complex, but it forms a coherent pattern. The work of Tomioka's group is particularly revealing.[16b] Photolysis of methyl diazoacetate (**1**, R = CH_3, Scheme 1) produces an excited singlet state (^{1}**1***) which can suffer Wolff rearrangement concurrent with nitrogen extrusion to yield ketene **3**, nitrogen loss and singlet carbene (**2S**) formation, or intersystem cross (ISC) to the triplet diazo compound (^{3}**1***). The singlet carbene and ketene intermediates are both trapped by alcohol, but to give different products, **4** and **5**, respectively (R′ = isopropyl, Scheme 1).[16b]

The triplet diazo excited state (^{3}**1***) can be quenched with isoprene when formed on direct photolysis of precursor. The triplet state of the diazo precursor can also be produced directly by photosensitization.[16] Reduction product **6** is clearly derived from a triplet state species, ^{3}**1*** or **2T** or both intermediates, because its yield is suppressed by isoprene and enhanced upon sensitization.[16b]

Ether **4** is still formed upon sensitized photolysis of **1** in alcohol, demonstrating that the triplet carbene **2T** can interconvert to the singlet state **2S**. This result is significant because Roth and Hutton have used low-temperature EPR spectroscopy to demonstrate that **2T** is the ground state of the carbene.[17] Thus, Tomioka's results show that the more reactive singlet state of carboethoxycarbene must be close in energy to the triplet ground state.[16] An MO calculation predicts that **2T** will be lower in energy that **2S** by 7 kcal/mol,[18] but this appears to be an overestimate.

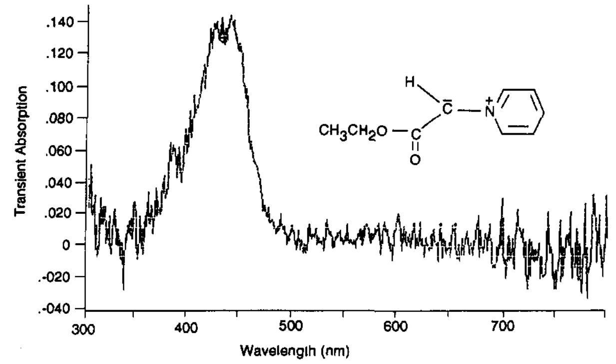


Figure 1. The transient spectrum of ylide **7** obtained by LFP of **1** in Freon-113 containing 3.3 M pyridine. The spectrum was recorded between 50 and 350 ns after the flash.

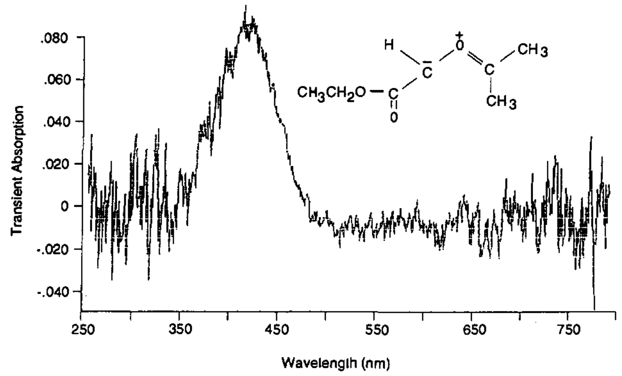


Figure 2. The transient spectrum of ylide **8** obtained by LFP of **1** in acetone. The spectrum was recorded between 50 and 350 ns after the flash.

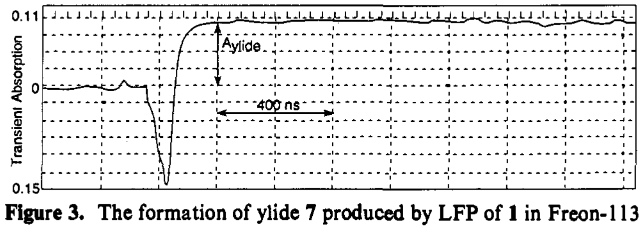


Figure 3. The formation of ylide **7** produced by LFP of **1** in Freon-113 containing 3.1 M pyridine. The region of negative absorption is due to scattered light from the laser pulse.

Wolff rearrangement product **5** is suppressed upon triplet sensitization of diazo precursor. This result demonstrates that any singlet carbene formed upon *direct* photolysis of precursor reacts with neat alcohol faster than it will undergo Wolff rearrangement.

III. Results

Laser flash photolysis (LFP, 351 nm, 17 ns) of EDA in alkanes, benzene, 1,1,2-trifluorotrichloroethane (Freon-113) or nitrile solvents fails to produce a UV–vis (300–700 nm) active transient intermediate. However, LFP of EDA in all of these solvents in the presence of either pyridine or acetone produces the transient spectra of Figures 1 and 2, respectively. The transients are attributed to pyridine and ketone ylides **7** and **8** respectively (Scheme 2) by trapping of singlet carbene **2S**, as per other carbene systems. The transients are formed within the 20-ns period of the laser pulse (Figure 3) such that $k_{growth} > 5 \times 10^7$ s^{-1}. The pyridine-derived transient has a lifetime of ≈40 μs, whereas the lifetime of the acetone-derived ylide is only 2.7 μs. These values

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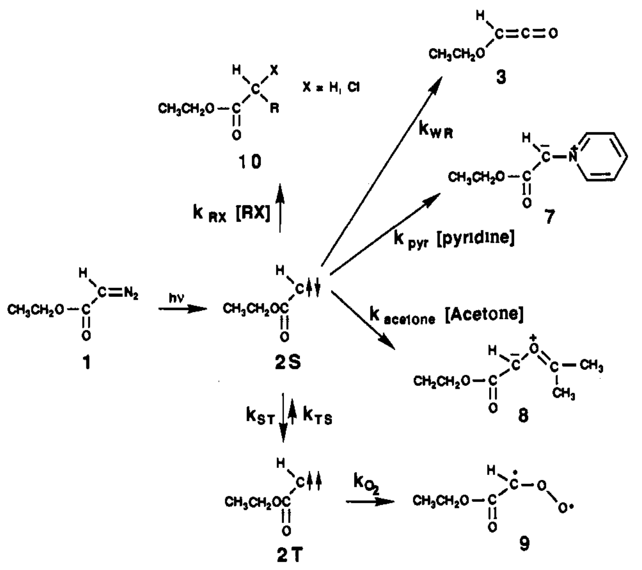
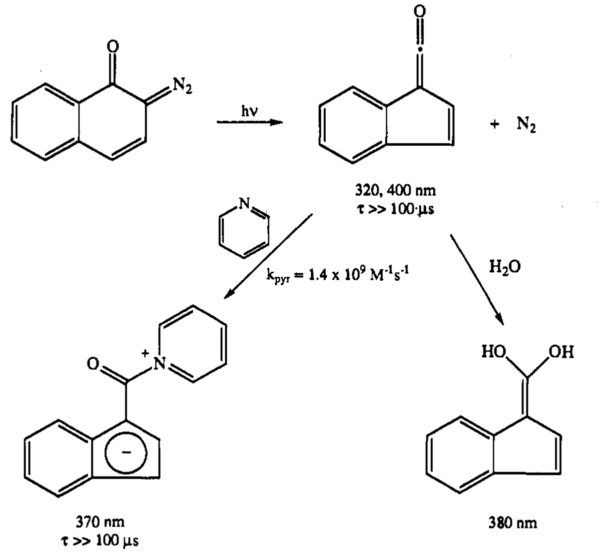
Scheme 2



Scheme 3



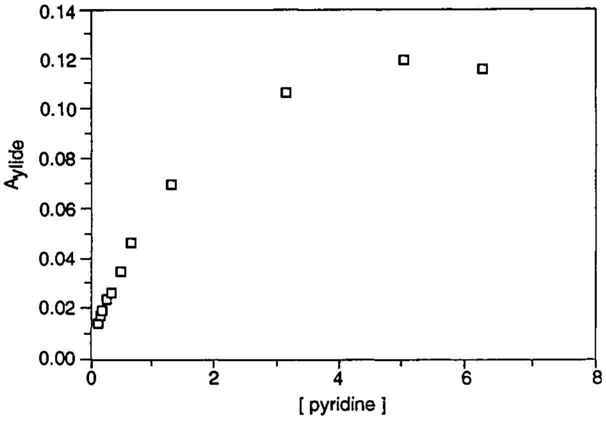


Figure 4. A plot of $A_{\text{ylide}}(7)$ versus [pyridine] in Freon-113.

compare well with those of other ketone and pyridine ylides which have been observed previously.[15]

Carbene or Ketene Ylides? Scaiano and co-workers have demonstrated that ketenes react with pyridine to form UV–vis active ylides[19] (Scheme 3). This immediately raises the concern that we might be trapping ketene 3 rather than singlet carbene **2S**. However based on Scaiano's[19] work, we expect that putative ketene 3 would have a lifetime in excess of 100 µs in the presence of dilute (<10^{-2} M) pyridine. The fact that upon direct photolysis the pyridine ylide of Figure 1 is formed faster than 20 ns in the presence of as little as 0.015 M pyridine excludes ketenes 3 as the precursor of the transient absorbing species.

It is not possible to generate a pyridine ylide when [pyridine] < 0.01 M. This is further evidence that pyridine is not trapping a long-lived (≈50–100 µs) transient. Furthermore, while acetone may well react with a ketene via a cycloaddition process, this reaction is not expected to produce a UV–vis active species. This is additional evidence against ketenes as precursors of the ylide probes of Figures 1 and 2. During the course of our work with ethyl diazoacetate, we have found no evidence for the formation of a ketene–pyridine ylide. Based on Scaiano's[19] work it is possible that the pyridine ylide of ketene 3 could be long-lived and have a chromophore in the UV–vis region of the spectrum. However, our studies[20] indicate that only cyclic ketenes produce detectable pyridine ylides. Thus, our failure to detect an ylide derived from 3 is consistent with our observations with other acyclic diazocarbonyl compounds.[20] The ylide band observed at 430 nm is more consistent with a carbene rather than a ketene origin.

Carbene or Diazo Excited-State Reaction with Pyridine? There is now considerable evidence that diazo excited states undergo intra- and intermolecular reactions which mimic carbene processes.[21] Thus, one must consider whether acetone and pyridine are trapping carbenes or excited states of the precursor. As both species are expected to be quite short lived (τ < 20 ns), we cannot use kinetics to immediately exclude either possibility. The issue will be decided later by comparing lifetimes deduced by direct and triplet sensitized laser flash photolysis. These results will demonstrate that the transient spectra have a carbene rather than an excited-state origin.

The Lifetime of Carboethoxycarbene. The optical yield of ylide (A_{ylide}) produced in a laser pulse is defined in Figure 3. In the absence of pyridine $A_{\text{ylide}} = 0$, but this quantity grows as the concentration of pyridine increases (Figure 4) until [pyridine] ≈ 4 M. Above 4 M pyridine in Freon-113, the ylide yield is saturated ($A^{\infty}_{\text{ylide}}$), implying that every carboethoxycarbene generated in the laser pulse is captured by pyridine or that $4k_{\text{pyr}} \gg k_{\text{wr}} + k_{\text{rx}}[\text{rx}]$ where k_{pyr}, k_{wr}, and k_{rx} are as defined in Scheme 2. As k_{pyr} is likely to be of the order of 10^9 M^{-1} s^{-1},[15] then $k_{\text{wr}} \ll 4 \times 10^9$ s^{-1} in 1,1,2-trichlorotrifluoroethane at ambient temperature.

The quantum yield ϕ_y of ylide formation is given in eq 1

$$\phi_{\text{ylide}} = \frac{\phi_c k_{\text{pyr}}[\text{pyridine}]}{k_{\text{wr}} + k_{\text{rx}}[\text{rx}] + k_{\text{pyr}}[\text{pyridine}]} \qquad (1)$$

where ϕ_c is the quantum yield of carbene formation. The optical yield of ylide is related to ϕ_{ylide} by eq 2.

$$A_{\text{ylide}} = \phi_{\text{ylide}} A^{\infty}_{\text{ylide}} \qquad (2)$$

Combining and rearranging eq 1 and 2 leads to eq 3:

$$\frac{1}{A_{\text{ylide}}} = \frac{k_{\text{wr}} + k_{\text{rx}}[\text{rx}]}{\phi_c A^{\infty}_{\text{ylide}}} \frac{1}{k_{\text{pyr}}[\text{pyridine}]} + \frac{1}{\phi_c A^{\infty}_{\text{ylide}}} \qquad (3)$$

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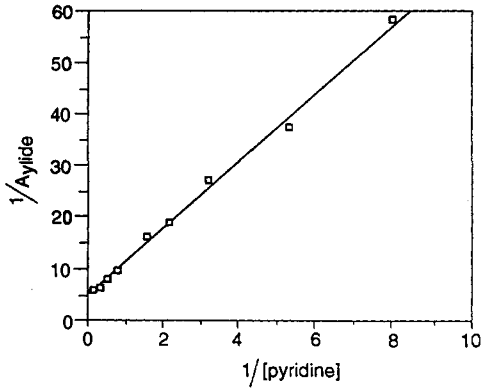


Figure 5. Double reciprocal treatment of the data of Figure 4.

Table 1. The Lifetime of Carboethoxycarbene in a Variety of Solvents

solvent	$k_{pyr}/\{k_{wr} + k_{rx}[rx]\}$[a]	lifetime (ns)[b,c]
1,1,2-trichlorotrifluoroethane	1.10	0.2–1.1
pentane	0.71	0.1–0.7
cyclohexane	0.50	0.1–0.5
cyclohexane-d_{12}	0.59	0.1–0.6
cyclopropyl cyanide	0.29	0.06–0.3
benzene	0.26	0.05–0.3
acetonitrile	0.18	0.04–0.2
acetonitrile-d_3	0.23	0.05–0.2

[a] Ratio of intercept/slope of double reciprocal plots. [b] Assuming $k_{pyr} = (1–5) \times 10^9\ M^{-1}\ s^{-1}$ and that $k_{wr} + k_{rx}[rx] \gg k_{isc}$. [c] Precision of ±10–15%.

Thus, a plot of ($1/A_{ylide}$) versus (1/[pyridine]) is predicted and found (Figure 5) to be linear. Division of the intercept by the slope of this plot gives the ratio $k_{pyr}/(k_{wr} + k_{rx}[rx])$ regardless of whether spin state equilibrium has been achieved and assuming that all of the decay process of the carbene proceeds through its singlet state. These ratios are given in Table 1 as a function of solvent. Values of k_{pyr} are expected to range between 1 and $5 \times 10^9\ M^{-1}\ s^{-1}$ for singlet carbene **2S** which indicates very large values of $k_{wr} + k_{rx}[rx]$ of $>10^9\ s^{-1}$. As ISC rates of singlet diphenylcarbene are on the order of $4 \times 10^9\ s^{-1}$,[22] our results indicate that spin relaxation of singlet carboethoxycarbene is likely to be incomplete in these solvents. If $k_{wr} + k_{rx}[rx] \gg k_{isc}$ then the singlet carbene lifetimes of Table 1 can be deduced.

The carbene lifetimes in cyclohexane and cyclohexane-d_{12} are very similar ($\tau_D/\tau_H = 1.0–1.3$). Singlet carbene CH insertion reactions with cyclohexane typically show isotope effects of $k_H/k_D = 2$.[22] The small isotope effects observed with carboethoxycarbene in this solvent indicate that reaction of the carbene with solvent by hydrogen atom abstraction or CH insertion does not substantially limit the lifetime of the carbene. In addition, these lifetimes are too short for carbene reaction with precursor to be significant. Thus, we feel that these lifetimes are substantially controlled by Wolff rearrangement and that $\tau \approx 1/k_{wr}$ in all of the solvents listed in Table 1.

The rate constant of reaction of chlorophenylcarbene with pyridine (k_{pyr}) is insensitive to solvent polarity.[23] If this is true as well for singlet carboethoxycarbene, then the lifetime of this carbene decreases with increases in solvent polarity. This would indicate that Wolff rearrangement is accelerated by solvent polarity as is 1,2-hydrogen migration.[24]

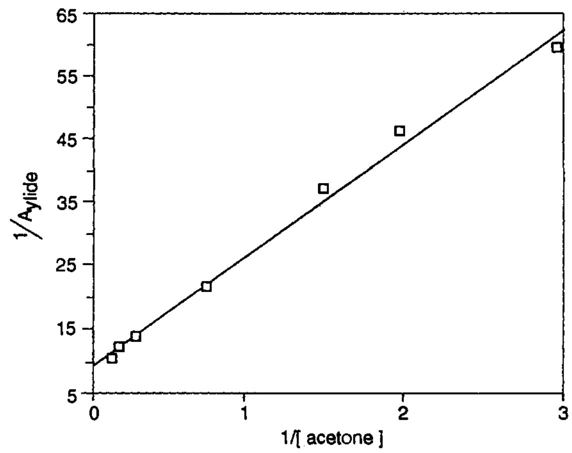


Figure 6. Double reciprocal treatment of the yield (A_{ylide}) of ylide **8** versus [acetone] in Freon-113.

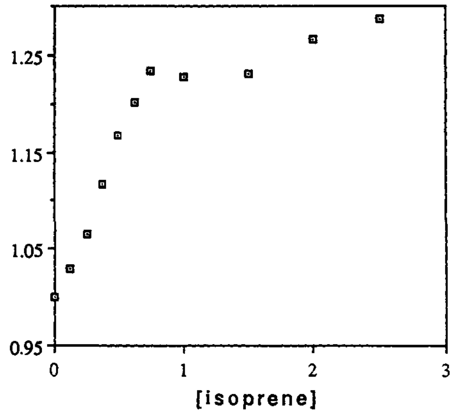
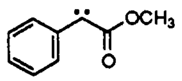


Figure 7. Stern–Volmer treatment of the quenching of ylide **8** yield (A_{ylide}) by isoprene upon LFP of **1** in acetone.

The yield of acetone ylide produced in Freon-113 also depends on the concentration of acetone. A plot of $1/A_{ylide}$ versus 1/[acetone] is linear (Figure 6) with $k_{acetone}\tau = 0.48$, deduced from the ratio of the intercept to slope of this plot. The results indicate that $k_{acetone} \approx {}^1/_{2k_{pyr}}$ or $(0.5–2.5) \times 10^9\ M^{-1}\ s^{-1}$.

The lifetimes of carboethoxycarbene that we have deduced are hundreds of times shorter than that of phenylcarbomethoxycarbene, which were directly measured by Fujiwara *et al.*[25]



The Triplet State of Ethyl Diazoacetate as a Source of Carbene. Tomioka's[16b] product studies clearly implicate the triplet state of methyl diazoacetate as a carbene precursor in both *direct* and sensitized photolysis of diazo precursor. To test the origin of the acetone trappable intermediate which produces a ylide, we studied the LFP of **1** in acetone in the presence of triplet quenchers.

The presence of either isoprene ($E_{triplet}$ = 59 kcal/mol)[26] or hexatriene ($E_{triplet}$ = 49 kcal/mol)[26] diminishes the yield of ylide **8** produced on LFP and EDA in acetone. With both quenchers, the yield of ylide smoothly decreases as the concentration of polyene increases from 0 to 1 M. Increases in polyene concentration above 1 M lead to only small decreases in ylide yield. Stern–Volmer treatments of the data are given in Figures 7 and 8.

These results are inconsistent with chemical quenching of the carbene precursor of the ylide. In such a case, the yield of ylide would continue to drop indefinitely with polyene concentration.

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[23] Jones, M. B.; Platz, M. S. *J. Org. Chem.* **1991**, *56*, 1694.

[24] Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966.

[25] Fujiwara, Y.; Tanimoto, Y.; Itoh, M.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **1987**, *109*, 1942.

[26] Murov, S.; Carmicheal, I.; Hug, G. L. *Handbook of Photochemistry*; Dekker: New York, 1993.

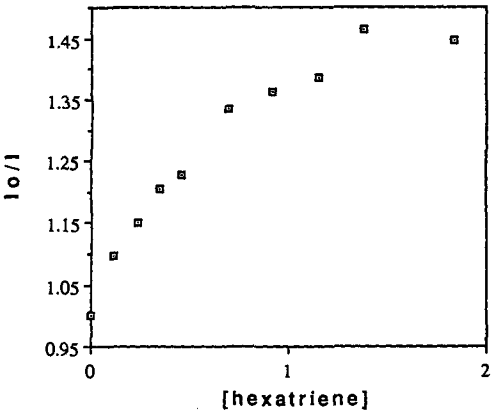


Figure 8. Stern–Volmer treatment of the quenching of ylide **8** yield (A_{ylide}) by hexatriene upon LFP of **1** in acetone.

The data are also inconsistent with consumption of diazo precursor by chemical reaction with polyene.

The results, we believe, are most consistent with trappable carbene generation proceeding from both singlet and triplet excited states of EDA and selective quenching of the ^{3}EDA route by isoprene or hexatriene. ^{3}EDA and some of the carbene/ylide ultimately derived from it are quenched between 0 and 1 M polyene. As all of the ^{3}EDA is quenched with 1 M polyene and as EDA does not react with polyenes at these concentrations, no further increase in quencher concentration leads to a reduction in ylide yield. (The carbene may slowly undergo chemical reaction with polyene because the slopes of the Stern–Volmer plots above 1 M alkene are small, but non-zero).

The yield of ylide is reduced by 20–25% by 1 M polyene. Thus, we conclude that 20–25% of the trappable carbene produced on photolysis of ethyl diazoacetate is derived from ^{3}EDA and that 75–80% of the trappable carbene originates from ^{1}EDA.

The Stern–Volmer plots shown in Figures 7 and 8 are linear between 0 and 0.8 M polyene with slopes of 0.33 ± 0.05 and 0.46 ± 0.05, respectively. The average of these slopes (0.4) corresponds to $k_q\tau$ where k_q is the rate constant of triplet energy transfer and τ is the lifetime of triplet EDA. As k_q is likely to be 10^{9-10} M^{-1} s^{-1}, the lifetime τ of ^{3}**1*** is estimated to be in the range of 40–400 ps in acetone at ambient temperature. Similar results were observed upon quenching the pyridine ylide with isoprene in Freon-113.

Triplet Sensitized Laser Flash Photolysis. A mixture of benzophenone (A_{351} = 1.0) and **1** (A_{351} = 0.16, [**1**] = 1.1 × 10^{-2}M) was flashed (351 nm) in deoxygenated Freon-113. Triplet benzophenone (λ_{max} = 535 nm) is completely quenched under these conditions. Sensitized flash photolysis under identical conditions but in the presence of pyridine produced a pyridine ylide. The yield of ylide (A_{ylide}) was dependent upon the concentration of pyridine. A double reciprocal treatment of the A_{ylide} data as a function of [pyridine] is linear (Figure 9). Division of the intercept by the slope of this plot yields the value $k_{pyr}\tau$ where $1/\tau$ is the sum of all rate constants of all processes which consumes the precursor of the ylide in the absence of pyridine.

Notice that $k_{pyr}\tau$ is the *same* (1 vs 2 ns) within experimental error for both direct and triplet photosensitized photolysis of EDA demonstrating that the ylide has the same immediate precursor in each mode. Recall that the triplet state of **1** cannot be the sole precursor of the pyridine ylide because the triplet quencher isoprene reduces the yield of ylide by only 20–25%. As the triplet state of **1** is not expected to reform the singlet excited state of **1**, ^{1}**1*** is excluded as the immediate precursor of pyridine ylide **7**. Thus, these experiments indicate that it is carboethoxycarbene and not a diazo excited state which reacts with pyridine to form the ylide detected.

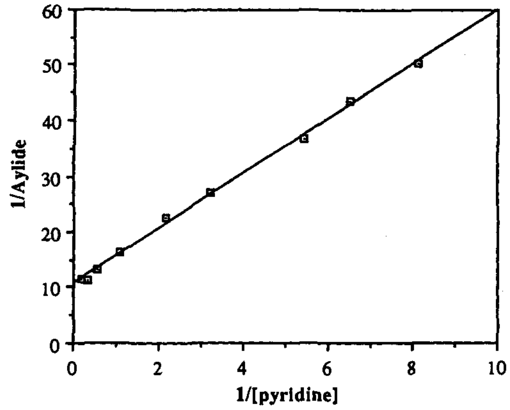
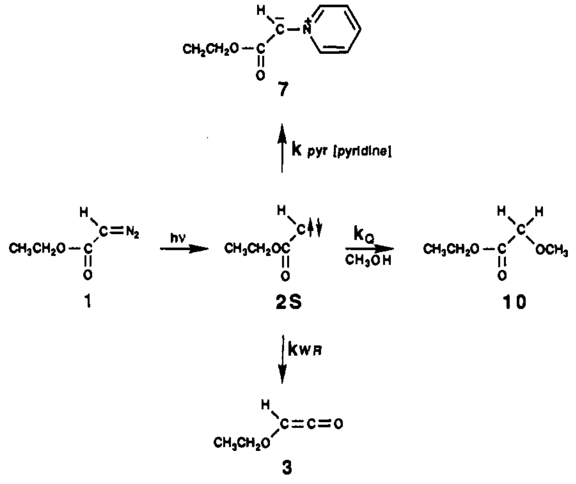


Figure 9. Double reciprocal treatment of the yield (A_{ylide}) of ylide **7** versus [pyridine] produced by benzophenone triplet sensitized LFP of **1** in Freon-113 containing pyridine.

Scheme 4

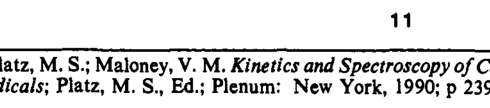


Reactions of Carboethoxycarbene with Representative Quenchers. The yield of ylide (A_{ylide}) in Freon-113 is saturated (A^∞_{ylide}) when [pyr] ≥ 4 M. Under these conditions, every carboethoxycarbene generated in a laser pulse is captured by pyridine and $1/\tau = k_{pyr}[\text{pyr}]$, with τ = 0.05–0.2 ns assuming k_{pyr} = (1–5) × 10^9 M^{-1} s^{-1}. In the presence of a second carbene quencher [Q] (Scheme 4), the yield of ylide is reduced such that eq 4 is valid.

$$\frac{A^{\infty}_{\text{ylide}}}{A_{\text{ylide}}} = 1 + \frac{k_q[\text{Q}]}{k_{\text{pyr}}[\text{pyr}]} \qquad (4)$$

Plots of $A^\infty_{\text{ylide}}/A_{\text{ylide}}$ versus [Q] are predicted and found (Figure 10) to be linear. Deduced values of k_q are listed in Table 2.

Similar experiments with a wider selection of carbene traps were performed in neat acetone. The data (Table 3) demonstrate that carboethoxycarbene reacts indiscriminantly with alcohols, ethers, alkenes, and dialkyl sulfides. Unlike other carbenes which have been studied by LFP techniques,[27] carboethoxycarbene reacts more rapidly with tetrahydrofuran (THF) than with methanol. Furthermore, the carbene reacts with THF and THF-d_8 with the same rate constant. Together, these results demonstrate, unsurprisingly,[11] that carboethoxycarbene reacts with THF by ylide formation.



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[27] Platz, M. S.; Maloney, V. M. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 239.

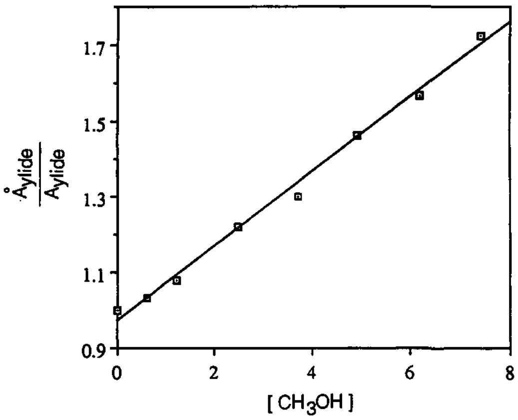


Figure 10. Stern–Volmer treatment of the quenching of the yield (A_{ylide}) of ylide **7** by methanol, produced by LFP of **1** in Freon-113 with 4.3 M pyridine.

Table 2. Stern–Volmer Quenching of the Carboethoxycarbene–Pyridine Ylide in Freon 113 with 4.3 M Pyridine

quencher	$k_q/\{k_{pyr}[pyr]\}^a$	$k_q{}^b$ (M^{-1} s^{-1})
methanol	0.19	$(0.82\text{–}4.1) \times 10^9$
cis-1,2-dichloroethylene	0.13	$(0.56\text{–}2.8) \times 10^9$
cyclohexene	0.13	$(0.56\text{–}2.8) \times 10^9$

[a] [pyr] = 4.3 M. [b] Assuming $k_{pyr} = (1\text{–}5) \times 10^9$ M^{-1} s^{-1}.

Table 3. Stern–Volmer Quenching of the Carboethoxycarbene–Acetone Ylide in Acetone

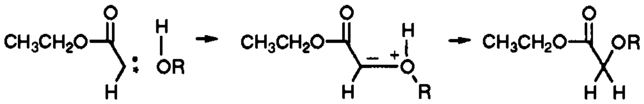
quencher	$k_q\tau^a$	$k_q{}^b$ (M^{-1} s^{-1})	k_H/k_D
dimethyl sulfide	0.23	$(1.6\text{–}7.8) \times 10^9$	
diethyl ether	0.19	$(1.6\text{–}6.5) \times 10^9$	
THF	0.17	$(1.2\text{–}5.8) \times 10^9$	1.1 ± 0.1
THF-d_8	0.16	$(1.1\text{–}5.4) \times 10^9$	
methanol	0.098	$(0.7\text{–}3.3) \times 10^9$	1.1 ± 0.1
methanol-*d*	0.091	$(0.6\text{–}3.1) \times 10^9$	
2-propanol	0.10	$(0.7\text{–}3.4) \times 10^9$	
cyclohexene	0.10	$(0.68\text{–}3.4) \times 10^9$	
cis-1,2-dichloroethylene	0.086	$(0.58\text{–}2.9) \times 10^9$	

[a] $1/\tau = k_{acetone}$[acetone]; neat[acetone] = 13.6 M. [b] Assuming $k_{acetone} = (0.5\text{–}2.5) \times 10^9$ M^{-1} s^{-1}.

Putative ylide **11** was not observed upon LFP of **1** in THF because it has either a very short lifetime or a very poor chromophore or both.

There is essentially no isotope OH(D) effect on the reaction of carboethoxycarbene with methanol. We have also found that carboethoxycarbene reacts with 2-propanol and methanol with essentially the same rate constant.

The alcohol and THF kinetic data support a mechanism of reaction of carboethoxycarbene with alcohols in which an ylide is formed irreversibly.



All of the absolute kinetic data obtained previously with arylcarbenes have pointed instead to a proton transfer mechanism.[27]

Trifluoroethanol reacts with acetone ylide **8**. the plot of k_{decay} of ylide **8** versus [CF$_3$CH$_2$OH] is not linear, but a linear plot is obtained when k_{decay} is plotted against [CF$_3$CH$_2$OH]^2. This indicates that carbonyl ylide **8** is reacting with a hydrogen bonded dimer of trifluoroethanol. The rapid reaction of ylide **8** with this dimer prevents our measurement of trifluoroethanol quenching of carboethoxycarbene.

IV. Conclusions

Laser flash photolysis of ethyl diazoacetate in hydrocarbons, Freon-113, and nitrile solvents generates singlet carboethoxycarbene which can be trapped with pyridine or acetone to form UV–vis active ylides. Study of the ylide yield as a function of acetone or pyridine concentration gives estimates of the carbene lifetime and the rate constants of Wolff rearrangement in various solvents. The rate of Wolff rearrangement is slightly accelerated by polar solvents. The carbene reacts indiscriminantly with alcohols, ethers, and alkenes. The carbene reacts with ethers and alcohols by ylide formation.

V. Experimental Section

Materials. Ethyl diazoacetate (containing ≤10% CH$_2$Cl$_2$) was used as received from Aldrich. Solvents (Aldrich) were also used as received unless otherwise specified. Pentane was stirred over concentrated sulfuric acid several times followed by an acid/permanganate solution before being dried over magnesium sulfate and distilled from P$_2$O$_5$. Benzene was distilled from sodium/benzophenone. Methanol was distilled from sodium. Acetonitrile was distilled from CaH$_2$. Pyridine was distilled and stored over KOH. Acetone was distilled from K$_2$CO$_3$. Isoprene, hexatriene, cyclohexene, 1,1,2-trichlorotrifluoroethane, and cyclopropyl cyanide were passed through an alumina column and used immediately.

Typical Procedure for Laser Flash Photolysis Experiments. The LFP apparatus in use at OSU has been described previously.[28] Stock solutions of **1** in dry solvent were typically prepared to an optical density of between 0.7 and 1.0 for lifetime experiments. A constant volume of the stock solution was added to Suprasil quartz cuvettes. (Typically, 10–12 cuvettes were used per experiment.) To each cuvette was added varying amounts of pyridine until [pyridine] ≈ 6 M. Solvent was then added to each cuvette in order to maintain a constant volume of sample throughout the experiment. Samples were degassed by purging with dry, oxygen-free argon for 2–3 min. Three transient spectra were recorded for each cuvette, with the average value of A_{ylide} used in the data analysis.

Stern–Volmer quenching experiments were performed similarly. Here, stock solutions consisted of EDA in acetone or in freon containing 4.3 M pyridine. Quencher concentrations were typically varied from 0 to between 3 and 6 M for a series of 8–10 cuvettes.

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(28) Soundarajan, N.; Platz, M. S.; Jackson, J. E.; Doyle, M. P.; Oon, S.-M.; Liu, M. T. H.; Anand, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 7143.