

Spectroscopic Detection of an Arylchlorocarbene–Ethyl Acetate Carbonyl Ylide and Subsequent Oxirane Formation

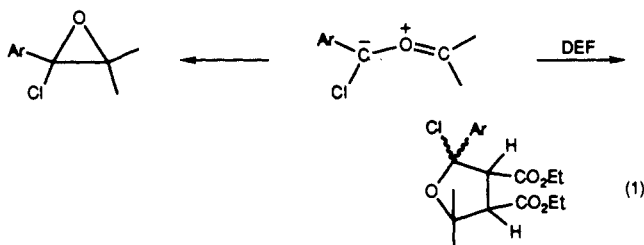
John E. Chateaufneuf* and Michael T. H. Liu†

Contribution from the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and Department of Chemistry, University of Prince Edward Island, Charlottetown, Canada C1A 4P3. Received October 22, 1990.
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Abstract: Laser flash photolysis of 3-chloro-3-(*p*-nitrophenyl)diazirine (**1**) generates the corresponding ground-state singlet carbene ($\lambda_{\max} = 310$ nm), which reacts with ethyl acetate to form a carbonyl ylide of the ester ($\lambda_{\max} = 490$ nm). The absolute rate constant for ylide formation in CH_2Cl_2 is $k = (2.85 \pm 0.17) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Subsequent cyclization of the ylide to the corresponding oxirane ($\lambda_{\max} = 350$ nm) occurs with a rate constant of $1.26 \times 10^6 \text{ s}^{-1}$ (21 °C) in ethyl acetate with Arrhenius activation parameters for oxirane formation of $E_{\text{act}} = 6.68 \pm 0.19 \text{ kcal/mol}$ and $\log A (\text{s}^{-1}) = 11.08 \pm 0.15$. The carbonyl ylide is also intercepted with the dipolarophile, diethyl fumarate, with a rate constant of $(1.04 \pm 0.07) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Additionally, solvent polarity effects on (*p*-nitrophenyl)chlorocarbene reactivity and spectroscopic evidence of oxirane formation ($\lambda_{\max} = 350$ nm) from the related acetone ylide of (*p*-nitrophenyl)chlorocarbene are presented.

Introduction

The formation of carbonyl ylides of arylcarbenes with simple esters is unprecedented, even though arylcarbene carbonyl ylides of ketones and aldehydes are quite common. For instance, carbonyl ylide formation of phenylchlorocarbene ($\text{Ph}\ddot{\text{C}}\text{Cl}$) with acetone and several of its para-substituted derivatives have been well documented.^{1–3} Product analysis has demonstrated that the carbonyl ylides are readily intercepted with diethyl fumarate (DEF), or in the absence of an ylide trap, may ring-close to the three-membered ring oxirane (eq 1). Laser flash photolysis (LFP)



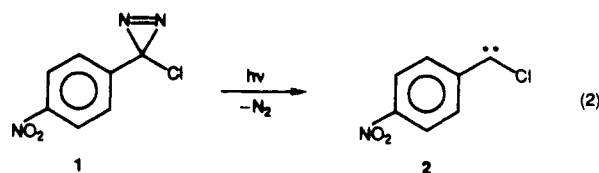
experiments have directly detected the transient absorption spectra of the phenylchlorocarbene–acetone ylide¹ ($\lambda_{\max} = 450$ nm) and the acetone ylides of the corresponding *p*-Cl,² *p*-CF₃,² and *p*-NO₂¹ derivatives, which have absorption maxima at 480, 480, and 590 nm, respectively. As expected, an increase in the electron-withdrawing ability of the para substituents facilitated ylide formation. Unexpectedly, however, attempts to observe carbonyl ylides of simple esters and carbonates have failed.⁴

Herein, we report the successful generation, detection, and absolute reactivity of the ethyl acetate carbonyl ylide of (*p*-nitrophenyl)chlorocarbene and spectroscopic detection of its subsequent oxirane formation. Further characterization of the unique reactivity of (*p*-nitrophenyl)chlorocarbene (*p*-NO₂Ph $\ddot{\text{C}}\text{Cl}$) is also presented.

Results

LFP of **1 in Isooctane.** The 355-nm LFP of a 1.77 mM solution of diazirine **1** (eq 2) in argon-saturated isooctane resulted in a UV absorption spectrum of *p*-NO₂Ph $\ddot{\text{C}}\text{Cl}$ (**2**), and absolute kinetics that are consistent with those previously reported⁵ for carbene **2**. The absorption spectrum was found to have an apparent maximum at 310 nm tailing to ca. 360 nm and no detectable visible absorption. An absolute bimolecular rate constant, k , of $(2.65 \pm 0.07) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained in the usual manner⁶ for the reaction of **2** with 2.53–36.8 mM tetramethylethylene (TME), which compares well with the previously obtained value⁵ of 2.9

$\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Carbene **2** was also found to react with 15.2–335 mM diethyl fumarate (DEF) in isooctane with $k = (9.66 \pm 0.40) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. No secondary transient species were observed as a consequence of this reaction.



LFP of **1 in Acetone.** LFP of 1.77 mM **1** in acetone as solvent resulted in the absorption spectrum of the acetone carbonyl ylide of **2** ($\lambda_{\max} = 590$ nm) as reported¹ (Figure 1). However, upon close examination of the time-resolved spectrum, a secondary absorption band ($\lambda_{\max} = 365$ nm) was found to be formed congruently with the decay of the carbonyl ylide (see Figure 1 inserts). Confirmation that the species responsible for the 365-nm absorption is a direct result of the acetone ylide of **2** was obtained with the addition of DEF. With addition of DEF the 365-nm transient “probed” the reactivity of the carbonyl ylide. That is, with the addition of DEF, the formation of the 365-nm signal accelerated, mimicking the 590-nm decay, with a simultaneous decrease in intensity at 365 nm. Unfortunately, the bimolecular rate constant for the reaction of the ylide with DEF could not be measured at 365 nm by the probe technique⁷ due to spectral overlap with the overwhelmingly strong signal of the acetone ylide. Nevertheless, considering the thoroughly investigated chemistry³ and spectroscopy^{1,2} for the reaction of the acetone ylide of **2** with DEF, the 365-nm absorption is assigned to the corresponding oxirane as formed in eq 1.

(1) Bonneau, R.; Liu, M. T. H. *J. Am. Chem. Soc.* **1990**, *112*, 744–747.

(2) Soundararajan, N.; Jackson, J. E.; Platz, M. S.; Liu, M. T. H. *Tetrahedron Lett.* **1988**, *29*, 3419–3422.

(3) (a) Liu, M. T. H.; Soundararajan, N.; Anand, S. M.; Ibata, T. *Tetrahedron Lett.* **1987**, *28*, 1011–1014. (b) Ibata, T.; Toyoda, J.; Liu, M. T. H. *Chem. Lett.* **1987**, *28*, 2135–2138.

(4) Platz et al. (ref 2) have pointed out that singlet carbene ylide formation with acetone and not with simple esters is inconsistent with a simple Lewis acid–base mechanism for ylide formation.

(5) Bonneau, R.; Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1989**, 510–512.

(6) Carbene kinetics were monitored at 320 nm for experimental convenience, i.e., greater A_0 . Bimolecular rate constants, k , were calculated from $k_{\text{exp}} = k_0 + k[s]$, where k_{exp} is the experimentally observed rate and k_0 is the rate of decay in the absence of substrates s . Errors represent $\pm 2\sigma$.

(7) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

† University of Prince Edward Island.

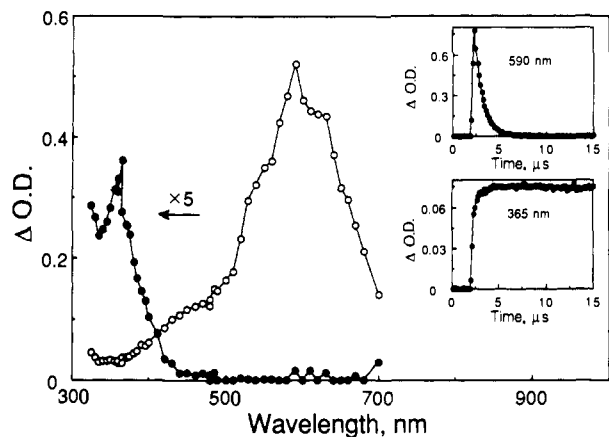


Figure 1. UV-visible absorption spectra observed 470 ns (O) and 13.6 μ s (●) after 355 nm LFP of 1.77 mM **1** in argon-saturated acetone. The 13.6- μ s spectrum is magnified by a factor of 5. Inserts demonstrate the time dependence observed at 590 nm (top) and 365 nm (bottom).

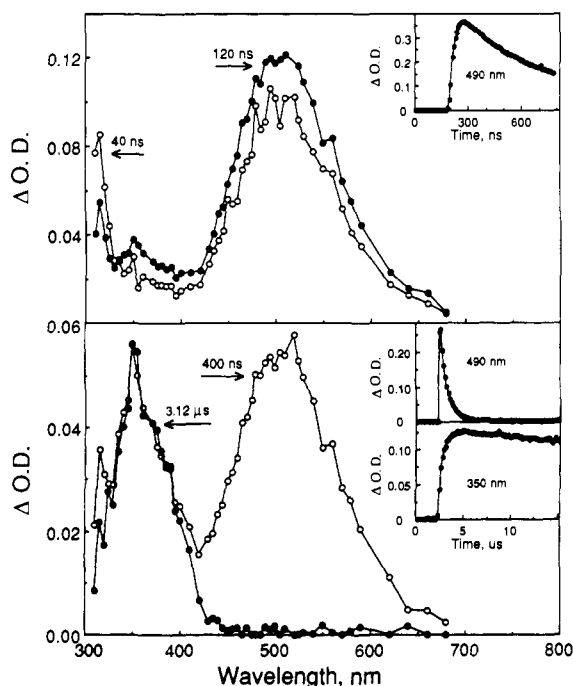


Figure 2. UV-visible absorption spectra observed 40 (O) and 120 ns (●) (top), and 0.4 (O) and 3.12 μ s (●) (bottom) after 355 nm LFP of 1.77 mM **1** in argon-saturated ethyl acetate. Inserts demonstrate typical time dependence observed at the indicated wavelengths.

LFP of **1 in Ethyl Acetate.** The LFP of **1** in EtOAc was strikingly similar to that observed in acetone. LFP of 1.77 mM **1** in argon-saturated EtOAc resulted in the observation of three distinct transient species. (1) Carbene **2** was formed within the excitation pulse and continued to be detected 40 ns after laser excitation of **1** (Figure 2, top) at 310 nm, although there was considerable overlap with secondary absorptions. (2) In EtOAc, LFP of **1** also resulted in a broad visible absorption band (Figure 2) ($\lambda_{\text{max}} = 490\text{--}520\text{ nm}$)⁸ that "grew-in" with a rate constant of $6.0 \times 10^7\text{ s}^{-1}$ (Figure 2, top, insert).⁹ It was apparent that the 490-nm band was due to the reaction of carbene **2** with EtOAc, although an absolute bimolecular rate constant was not measurable at 320 nm due to overlapping transient absorptions. It was possible, however, to measure the rate constant of formation of the 490-nm band in CH_2Cl_2 (see Discussion for choice of solvent)

(8) All ylide kinetics were monitored at 490 nm; hence, this species will be referred to hereafter as the 490-nm band.

(9) It should be noted that the insert traces were recorded under slightly different experimental conditions from the time-resolved spectrum, e.g., laser intensity and focus, resulting in differences in absolute $\Delta\text{O.D.}$ values.

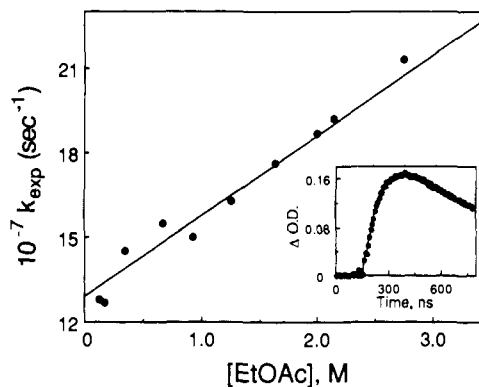


Figure 3. Plot of k_{exp} vs [EtOAc] obtained by monitoring growth of ylide **3** at 490 nm in CH_2Cl_2 . Insert demonstrates growth ($1.87 \times 10^7\text{ s}^{-1}$) observed with 2 M ethyl acetate.

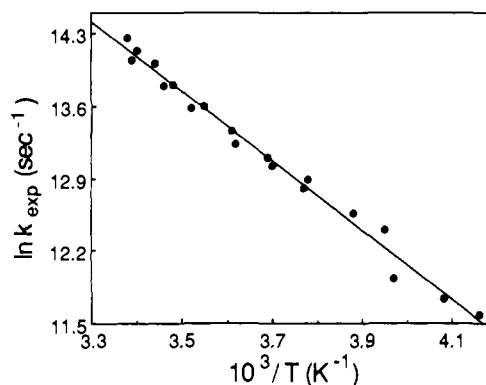


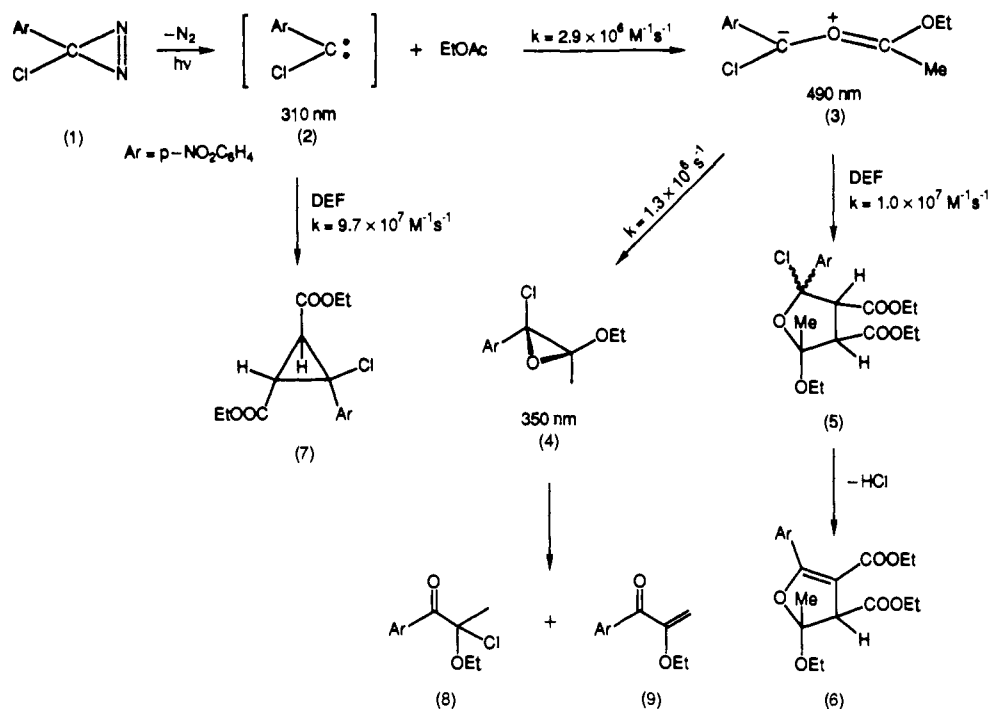
Figure 4. Arrhenius plot obtained by measuring the rate of decay of ylide **3** in ethyl acetate at 490 nm.

with added EtOAc. A bimolecular "quenching" plot for the reaction of carbene **2** with EtOAc (Figure 3) resulted in a rate constant for the formation of **3** of $(2.85 \pm 0.17) \times 10^6\text{ M}^{-1}\text{ s}^{-1}$. Confirmation that the 490-nm growth was probing the kinetics of carbene **2** was obtained by measuring growth rate constants at 490 nm in CH_2Cl_2 containing an experimentally optimum "probe" concentration of 2 M EtOAc (see insert, Figure 3) with the addition of 2.52–20.1 mM TME. This resulted in a bimolecular rate constant for the reaction of carbene **2** with TME of $(1.69 \pm 0.15) \times 10^9\text{ M}^{-1}\text{ s}^{-1}$, as calculated by $k_{\text{exp}} = k_0 + k[\text{EtOAc}] + k[\text{TME}]$. In neat EtOAc at room temperature, the visible absorption band decayed with first-order kinetics at a rate of $1.26 \times 10^6\text{ s}^{-1}$. The temperature dependence (22.6 to $-33\text{ }^\circ\text{C}$) of the 490-nm decay (Figure 4) resulted in Arrhenius activation parameters of $E_{\text{act}} = 6.68 \pm 0.19\text{ kcal/mol}$ and a preexponential factor of $10^{11.08 \pm 0.15}$. As was the case in acetone, the visible absorption band decayed with the concomitant growth of another transient species. (3) An absorption band at 350 nm that "grew-in" as a result of the 490-nm band (Figure 2, bottom, inserts) possessed a millisecond lifetime and "probed" the kinetics of the 490-nm band. Addition of DEF decreased the lifetime of the 490-nm band while it simultaneously decreased the growth lifetime of the 350-nm band. The overall intensity of the 350-nm band also decreased with added DEF. "Quenching" of the 490-nm band in EtOAc with DEF (1.62 mM–1.32 M) in a flow-cell system resulted in a bimolecular rate constant of $(1.04 \pm 0.07) \times 10^7\text{ M}^{-1}\text{ s}^{-1}$. Although the 350-nm band qualitatively "probed" the kinetics of the 490-nm transient, measuring the rate constant at 350 nm was impossible due to interference with the visible absorption band.

Discussion

The products observed^{1,3} in the thermal decomposition of **1** in the presence of acetone had led to a mechanistic scheme that involved reaction of singlet $p\text{-NO}_2\text{Ph}\ddot{\text{C}}\text{Cl}$ (**2**) with acetone to form a carbonyl ylide that, in the absence of an ylide trap, would ring-close to a putative 2-chlorooxirane. Previous LFP experiments

Scheme I



have helped confirm this mechanism by detection of the carbonyl ylide. In this work, we further support this scheme by detection of a product species at 365 nm (Figure 1) that is formed from the decay of the acetone ylide and is assigned to the 2-chloro-oxirane.

Product analysis of the decomposition of 1 in the presence of EtOAc was very similar to that observed in the presence of acetone and is consistent with the reactivity outlined in Scheme I. Chemical evidence of the existence of ylide 3, formed by reaction of carbene 2 with EtOAc, was readily obtained from the retrieval and identification of 6. Furan 6 is the HCl elimination product of the dipolar cycloaddition adduct 5, which is formed from the interception of ylide 3 with DEF. In the presence of DEF, carbene 2 undergoes cycloaddition to DEF to form cyclopropane 7 in competition with ylide formation. Decomposition of 1 in EtOAc as solvent containing 4 mM DEF resulted in a product ratio of 1:4.3 for 6 and 7. In the absence of DEF, oxirane 4 formation was confirmed by the identification of ketone 9, the HCl elimination product of ketone 8. The two major preparative photolysis products of 1 in EtOAc (see the Experimental Section) are the corresponding benzal chloride and benzaldehyde. The exact origins of these products are unknown.¹⁰ However, similar products have been observed in the decomposition of 1 and phenylchlorodiazirine in acetone¹ and in isooctane.¹¹

The dramatic similarities between LFP observations of 1 in EtOAc and those in acetone further support Scheme I and, in conjunction with the product analysis, lead to our assignment of the broad visible absorption band (490 nm, Figure 2) to the ethyl acetate carbonyl ylide (3) of carbene 2, and assignment of the 350-nm band to the subsequently formed oxirane (4).

In order to determine the importance of reversibility in the formation of ylide 3, it is helpful to compare the present results with those reported for the formation of the acetone ylides of carbene 2 and PhC̄Cl. Relative kinetic measurements determined that the reverse reaction of carbene 2 with acetone was insignificant.³ This was spectroscopically supported by the observation¹

of a (*p*-nitrophenyl)chlorocarbene-acetone ylide lifetime that was independent of acetone concentration in isooctane. In contrast, the lifetime of the acetone ylide of PhC̄Cl is dramatically shortened with an increase in acetone concentration and indicates significant reversibility to singlet carbene. The lifetime of ylide 3 in isooctane was found to be independent of EtOAc concentration when EtOAc was added in substrate concentrations, i.e. <3 M.

Comparison of the Arrhenius activation parameters for the decay of ylide 3, $E_{\text{act}} = 6.68 \text{ kcal/mol}$ and $\log A = 11.08 \text{ s}^{-1}$, with the parameters for the decay of the acetone ylide of carbene 2, $E_{\text{act}} = 5.90 \text{ kcal/mol}$ and $\log A = 10.30$, indicate similar decay mechanisms. Although A factors appear low for a unimolecular reaction, one expects a considerable loss in entropy in the cyclization process. In contrast, the extremely low values of $E_{\text{act}} = 2.1 \text{ kcal/mol}$ and $\log A = 7.40$ for the decay of phenylchlorocarbene-acetone ylide clearly demonstrate additional deactivation pathways to unimolecular decay. The ability to quench ylide 3 with DEF with the simultaneous and strongly competing cyclopropanation reaction of 2 with DEF, and the ability to use the growth of ylide 3 as a probe to measure the very rapid reaction of 2 with TME further indicate that reversion of ylide 3 to carbene 2 and EtOAc is insignificant.

It is not clear why arylcarbenes form carbonyl ylides with ketones and not esters.⁴ It is, however, understandable why the ester ylide of the parent PhC̄Cl is not observed by nanosecond LFP considering the absolute reactivities involved. The reaction of PhC̄Cl with acetone is 175 times slower than that of 2 with acetone. A comparison with the bimolecular rate constant of $2.85 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for reaction of 2 with EtOAc yields $k < 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for PhC̄Cl with EtOAc, assuming similar differences in reactivity toward EtOAc. On the other hand, a similar comparison with *p*-ClPhC̄Cl and *p*-CF₃PhC̄Cl would give reactivities in the 10^5 – $10^6 \text{ M}^{-1} \text{ s}^{-1}$ range, which might be observed in the nanosecond regime. The observed reactivity of 2 with EtOAc may, therefore, indeed be unique to 2. Carbene 2 has been observed to undergo anomalous behavior for a ground-state singlet. Carbene 2 is designated as a ground-state singlet due to stereospecific addition to olefins (e.g., (*Z*)-4-methyl-2-pentene)¹¹ and lack of a low-temperature EPR signal.⁵ However, 2 would appear to undergo the spin-forbidden reaction with molecular oxygen to form carbonyl oxide, $\lambda_{\text{max}} = 400 \text{ nm}$.¹¹

During these investigations, another interesting phenomenon was observed, namely, a solvent polarity effect on the reactivity

(10) A likely source of the benzal chloride is reaction of carbene 2 with HCl generated during the formation of 6 and 9. Also, 2 can react with trace H₂O to give chlorohydrin with subsequent loss of HCl to yield the benzaldehyde (ref 11). These products may also be generated during workup.

(11) In the presence of oxygen additional absorptions were observed ranging from 380 to 480 nm. Also see: Liu, M. T. H.; Bonneau, R.; Jefford, C. W. *J. Chem. Soc., Chem. Commun.* 1990, 1482–1483.

Table I. Dependence of Growth and Decay Lifetimes^a of Ylide 3 in Various Solvent Mixtures

% ethyl acetate	cosolvent	growth τ (ns)	decay τ (ns)
90	isooctane	18.2	462
30	isooctane	8.6	377
90	carbon tetrachloride	16	268
30	carbon tetrachloride	6.6	295
90	chloroform	17	257
30	chloroform	26	449
90	methylene chloride	21	283
30	methylene chloride	50	609

^a Monitored at 490 nm in argon-saturated solutions at 21 ± 2 °C.

of 2.¹² Initial attempts to measure the rate of growth of ylide 3 with added EtOAc in isooctane were unsuccessful. Surprisingly, a decreased growth rate was observed at 490 nm with an increase in EtOAc molarity. With the relatively large quantities of EtOAc required to generate ylide 3, the change in solvent composition became suspect. The possibility that differences in solvent polarity were influencing the reactivity of 2 was tested by measuring the absolute kinetics for reaction of 2 with TME at 320 nm in several "inert" solvents. Rate constants of $(2.65 \pm 0.07) \times 10^9$ (1.12 ± 0.03) $\times 10^9$, $(9.93 \pm 0.31) \times 10^8$, and $(8.65 \pm 0.27) \times 10^8$ M⁻¹ s⁻¹ in isooctane, CCl₄, CH₂Cl₂, and CHCl₃, respectively, demonstrated a small but measurable difference in the reactivity of 2.¹² A more dramatic effect on carbene 2 reactivity was reflected in the growth lifetimes of ylide 3 in mixtures of EtOAc and inert cosolvents. These data with the decay lifetime of ylide 3 are presented in Table I. A "stabilizing effect" is observed on the carbene lifetime when EtOAc is the major solvent component with isooctane and CCl₄ as cosolvents, whereas the opposite is observed with CHCl₃ and CH₂Cl₂ as cosolvents. The degree of "stabilization" observed for both carbene and ylide coincides with empirical polarity parameters¹³ based on kinetic measurement, as well as the solvent polarity parameter $E_T(30)$, where the following solvents are listed¹³ in decreasing "polarity": CH₂Cl₂ > CHCl₃ > EtOAc > CCl₄ > hexane. Therefore, in the more "polar" solvent, CH₂Cl₂, the rate constant for the reaction of 2 with EtOAc could be measured since addition of EtOAc as substrate resulted in a change in carbene 2 lifetime that represented chemical reactivity and not stabilization due to solvent.¹⁵ With this in mind, the "true" rate constant for the reaction of 2 with EtOAc in isooctane could be considerably larger than that measured in CH₂Cl₂.^{12b}

In conclusion, unique carbenic reactivity has been observed in the reactivity of *p*-NO₂PhCCl. Among them are ester ylide

(12) (a) Similar solvent polarity effects have been observed in the reaction of PhCCl with olefins: Soundararajan, 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*, 7143-7152. (b) Also, reaction of PhCCl with pyridine is ~2.5 times greater in hexane than in EtOAc: Platz, M. S. Private communication.

(13) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH Verlagsgesellschaft: Weinheim, 1988; pp 352, 363-375. The $E_T(30)$ values are: CH₂Cl₂ (40.7); CHCl₃ (39.1); EtOAc (38.1); CCl₄ (32.4) and hexane (31.0).

(14) Liu, M. T. H.; Toriyama, K. *Can. J. Chem.* **1972**, *50*, 3009-3016.

(15) This does not preclude stabilization of carbene 2 in the more polar solvents. This is potentially measurable from k_0 (ref 6); however, k_0 also reflects reactivity of 2 with trace impurities, which may be independently dependent on solvent polarity.

formation, reaction with oxygen, and solvent polarity effects. Both direct and indirect results demonstrate formation of an ethyl acetate ylide and its resulting oxirane. Also, spectroscopic detection of the putative 2-chlorooxirane from the acetone ylide of *p*-NO₂PhCCl has been presented.

Experimental Section

Materials. 3-Chloro-3-(*p*-nitrophenyl)diazirine (1) was prepared¹⁴ by the oxidation of the *p*-nitrobenzamidinium hydrochloride in a freshly prepared solution of sodium hypochlorite in DMSO. The following solvents and substrates were used as received: ethyl acetate (Fisher); ethyl acetate (B & J brand high-purity solvents, ketone free); acetone and methylene chloride (Fisher, spectroanalyzed); isooctane (2,2,4-trimethylpentane) and carbon tetrachloride (Aldrich, spectrophotometric grade); acetonitrile (Fisher, HPLC grade); and diethyl fumarate (Aldrich, 98%). Chloroform (Aldrich, spectrophotometric grade) was passed through alumina and distilled from K₂CO₃ to remove amylene stabilizers, and tetramethylethylene (2,3-dimethyl-2-butene) (Aldrich, 99+%) was distilled prior to use.

Laser Flash Photolysis. Unless otherwise stated, LFP experiments were carried out in 9 × 6 mm² Suprasil quartz cells containing 2 mL of argon-deaerated solution at room temperature (21 ± 2 °C). Perpendicular 355-nm laser excitation (~8 mJ, pulse width ~6 ns) from a Quanta Ray DCR-1 Nd:YAG laser system was used with a 1000-W pulse xenon lamp as the monitoring source. The flash photolysis apparatus used is as previously described,¹⁶ with the exception of the computer analysis, which is now performed on a VAX-11/780. Variable-temperature experiments were performed by passing liquid N₂-cooled N₂ through a quartz vacuum jacket, which encompassed both the sample cell and cell holder. Temperatures were stabilized to ± 0.2 °C prior to each kinetic experiment.

Preparative Photolysis. A solution of 1 (2 mmol) in 4 mL of ethyl acetate under N₂ atmosphere was sealed in a 8-mm diameter Pyrex tube. The tube was immersed in a constant-temperature water-jacketed bath made of Pyrex glass thermostated to 25 °C by external circulation of water and photolyzed for 4 h in a Rayonet photoreactor using a battery of 350-nm UV lamps. The products were as follows: 25% *p*-NO₂C₆H₄CHO; 50% *p*-NO₂C₆H₄CHCl₂; and 25% ketone 9 (MS *m/e* 221 (2, M⁺), 176 (100)). Irradiation of 1 (2 mmol) in 4 mL of ethyl acetate mixed with an appropriate amount of diethyl fumarate (4 mmol) was photolyzed under similar conditions to give 20% *p*-NO₂C₆H₄CHCl₂, 65% cyclopropane 7: MS *m/e* 341 (1, M⁺), 268 (100); ¹H NMR (CCl₄) δ 1.12 (t, $J = 6$ Hz, ester CH₃), 1.33 (t, $J = 6$ Hz, 3 H, ester CH₃), 3.05 (s, 2 H, cyclopropane hydrogens), 3.95 (q, $J = 6$ Hz, 2 H, ester CH₂), 4.28 (q, $J = 6$ Hz, 2 H, ester CH₂), 8.12-8.48 (m, 4 H, aromatic hydrogens); and 15% furan 6 (MS *m/e* 393 (3, M⁺), 273 (100), 246 (33), 150 (58)). Products 6 and 9 are stable at room temperature but decomposed in the silica gel during column chromatography.

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Supplementary Material Available: Tables II and III containing kinetic data used to calculate bimolecular rate constants that were not presented graphically (2 pages). Ordering information is given on any current masthead page.

(16) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330-2335.