

## Cyclopropyl-, Cyclopropylmethyl-, and Dicyclopropylcarbenes

David A. Modarelli and Matthew S. Platz\*

Department of Chemistry, The Ohio State University  
120 West 18th Avenue, Columbus, Ohio 43210

Robert S. Sheridan\* and Jeff R. Ammann

Department of Chemistry  
The University of Nevada  
Reno, Nevada 89557

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Laser flash photolysis (LFP) is now an established tool for the study of the intermolecular reactions of arylcarbenes.<sup>1</sup> The aromatic chromophore facilitates direct detection of the carbene. While it is possible to directly observe the transient spectra of certain alkylhalo- and alkylalkoxycarbenes in solution,<sup>2</sup> trapping the carbene with pyridine generates a long-lived, intensely absorbing ylide whose properties are ideal for kinetic analysis.<sup>3</sup> The pyridine ylide probe method has enabled the study of intermolecular and, more recently, intramolecular reactions of alkyl-, alkylchloro-, and dialkylcarbenes.<sup>2,3,5</sup> Herein we are pleased to report the study of cyclopropyl-, cyclopropylmethyl-, and dicyclopropylcarbenes by the probe method. Cyclopropylcarbene is of special interest because of its remarkable rearrangement to cyclobutene, a process discovered by Shechter and Friedman (Scheme I),<sup>4</sup> and because of the possibility of overlap between a Walsh orbital of cyclopropane with an empty p-orbital of the singlet carbene.<sup>6</sup>

LFP (XeF, 351 nm, 55 mJ, 17 ns) of cyclopropyldiazirine (**1**) in pentane at 25 °C fails to produce a detectable transient absorption. However, LFP of **1** in pentane containing pyridine produces a transient spectrum ( $\lambda_{\max} = 379$  nm) attributed to ylide **3** by analogy to the spectra of other carbene-pyridine ylides.<sup>3,5</sup> The yield of ylide increases with increasing [pyridine] as shown in Figure 1 but is saturated ( $A_y^{\text{sat}}$ ) when [pyridine] > 0.2 M. At these pyridine concentrations, all of the cyclopropylcarbene produced in a laser flash is captured. Cyclopropylmethylcarbene can be detected and trapped as per cyclopropylcarbene.

Scheme I predicts eq 1,<sup>5</sup> where  $A_y$  is the optical yield of ylide produced in a laser pulse,  $\phi_c$  is the quantum yield of carbene formation,  $k_{\text{pyr}}$  is the rate constant for reaction of carbene with pyridine, and  $\tau$  is the carbene lifetime in the absence of pyridine.

$$\frac{1}{A_y} = \frac{1}{\phi_c A_y^{\text{sat}}} + \left( \frac{1}{\phi_c A_y^{\text{sat}}} \right) \left( \frac{1}{k_{\text{pyr}} \tau} \right) \left( \frac{1}{[\text{pyr}]} \right) \quad (1)$$

A plot of  $1/A_y$  versus  $1/[\text{pyr}]$  is linear (Figure 2), and division of the slope by the intercept of this plot yields values of  $k_{\text{pyr}}\tau$ . Values of  $\tau$  are listed in Table I and are obtained by assuming

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(4) (a) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002. (b) Shevlin, P. B.; Wolf, A. P. *J. Am. Chem. Soc.* **1966**, *88*, 4735. (c) Chang, K. T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082.

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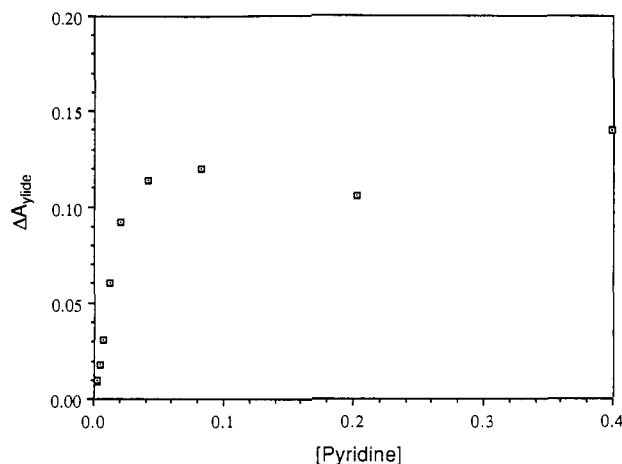


Figure 1. Plot of the optical yield ( $A_{\text{ylide}}$ ) of ylide **3** in pentane at 25 °C as a function of pyridine.

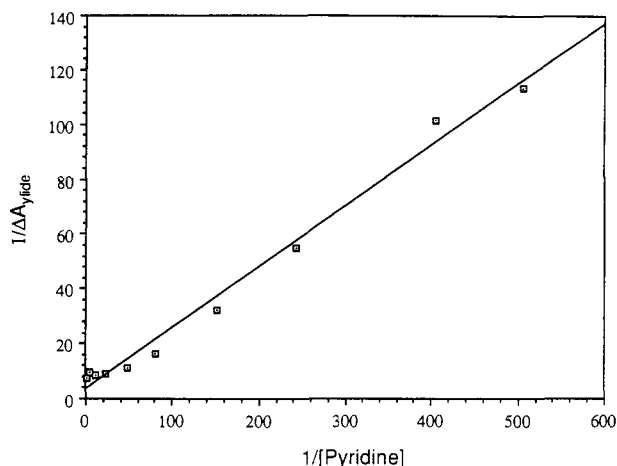
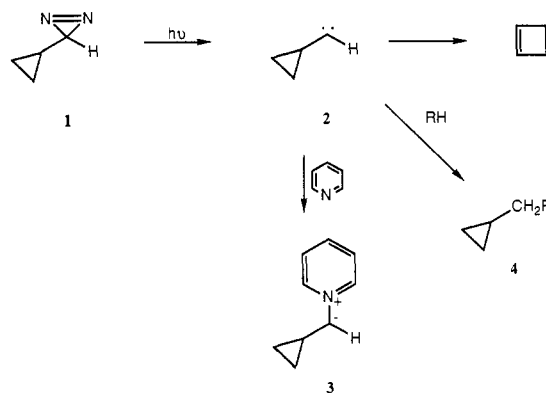


Figure 2. Double reciprocal treatment of the data of Figure 1.

### Scheme I



that  $k_{\text{pyr}} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and is independent of solvent, as demonstrated for other carbenes.<sup>3,7</sup>

Dicyclopropyldiazirine (**5**)<sup>8</sup> and dicyclopropylcarbene (**6**) were studied as per the study of cyclopropylcarbene. However, in this case a transient was observed ( $\lambda_{\max} = 235$  nm) in pentane in the

(7) This analysis assumes that cyclopropylcarbene and cyclopropylmethylcarbene have singlet ground states or very accessible singlet states at ambient temperature.

(8) Ammann, J. R.; Subramanian, R.; Sheridan, R. S. *J. Am. Chem. Soc.* **1992**, *114*, 7592.

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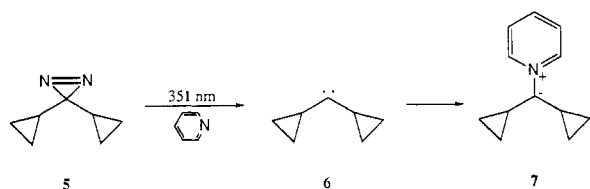
(10) Moss, R. A.; Ho, G. J.; Liu, W. *J. Am. Chem. Soc.* **1992**, *114*, 959.

**Table I.** Lifetimes of Cyclopropyl-Substituted Carbenes in Solution at or near 25 °C

carbene	solvent	lifetime <sup>a</sup>
	pentane	0.5 <sup>c</sup>
	pentane	22 <sup>c</sup>
	pentane	24
	cyclohexane	14
	cyclohexane- <i>d</i> <sub>12</sub>	21
	acetonitrile- <i>d</i> <sub>3</sub>	14
	chloroform- <i>d</i>	4
	pentane	21
	pentane	22
	pentane	32 <sup>b</sup>
	isooctane	1100–2300 <sup>d</sup>
	pentane	7142 <sup>e</sup>

<sup>a</sup> Assuming  $k_{\text{pyr}} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>b</sup> Direct detection of the carbene. <sup>c</sup> Reference 5. <sup>d</sup> Reference 9. <sup>e</sup> Reference 10.

absence of pyridine. This transient is attributed to carbene **6** because of its obvious similarity to the spectrum of **6** recorded in a nitrogen matrix.<sup>8</sup> Ylide **7** was also detected in a pentane



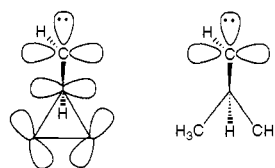
solution containing pyridine. The lifetimes determined with use of the pyridine ylide method and by direct detection are shown in Table I and are in good agreement. The lifetime determined by analysis of the decay of the carbene at 235 nm is more accurate than the value deduced from monitoring the ylide signal because it does not depend on an estimated value of  $k_{\text{pyr}}$ . The lifetimes of **6** determined by direct observation and with use of the probe method are similar, which validates our assumptions concerning  $k_{\text{pyr}}$ .

The lifetimes of the three carbenes of this study are shown to be equivalent within experimental error and the same as that of dimethylcarbene.<sup>5</sup> The isotope effect of 1.5 on the lifetimes of cyclopropylcarbene in cyclohexane-*d*<sub>12</sub>/cyclohexane reveals that the cyclopropylcarbene lifetime is substantially controlled by reaction with solvent as is the lifetime of dimethylcarbene.<sup>5</sup> This conclusion is supported by GC-MS analysis of the products formed

upon extended photolysis of cyclopropyldiazirine in cyclohexane. Substantial amounts of carbene-cyclohexane adduct is produced along with a small amount of azine. Complete details of this study will be reported later.

Surprisingly, the addition of a second cyclopropyl group  $\alpha$  to the carbene center does not stabilize the carbene kinetically; it does not influence the carbene lifetime. This observation is in striking contrast to the results obtained with cyclopropylchloro- and cyclopropylfluorocarbene, where the presence of a halogen atom  $\alpha$  to the carbene center dramatically extends the carbene lifetime (Table I). Replacement of a hydrogen atom by a methyl group on the cyclopropyl carbene center does not influence the lifetime of the carbene. Thus the total rate of all possible intermolecular reactions and intramolecular rearrangements of cyclopropyl-, cyclopropylmethyl-, dicyclopropyl-, and dimethylcarbene are comparable.

Overlap of the empty p-orbital of singlet cyclopropylmethylcarbene with the Walsh orbital of cyclopropane does not kinetically stabilize the carbene relative to dimethylcarbene, the parent dialkylcarbene. However, a comparison restricted only to alkylcarbenes reveals that cyclopropylcarbene is much longer lived than methylcarbene-*d*<sub>4</sub>, perhaps due to electronic stabilization of the carbene by the cyclopropane ring or to the unusually strong carbon-hydrogen bond strength in cyclopropylcarbene. In any case, carbon-carbon migration in cyclopropylcarbene is slower than deuterium migration in methylcarbene-*d*<sub>4</sub>.



Sheridan, Ammann, and Subramanian<sup>8</sup> have demonstrated that dicyclopropylcarbene has a singlet ground state. The common lifetimes of cyclopropyl-, cyclopropylmethyl-, and dicyclopropylcarbene (**6**) implies that the singlet states of cyclopropylcarbenes and cyclopropylmethylcarbenes are as accessible as that of **6** and are either the ground states for these carbenes or within 1 kcal/mol of the ground states.

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**Supplementary Material Available:** Transient spectra of ylide **3** and dicyclopropylcarbene (2 pages). Ordering information is given on any current masthead page.