and the kinetic behavior of the ylide, 3, is given by

$$[3]_t = Y_m[\exp(-t/\tau_2) - \exp(-t/\tau_1)] \qquad (1)$$

where $1/\tau_2 = k_q$[olefin], $1/\tau_1 = k_i + k_y$[pyridine] + k_c[olefin], and Y_m is the amount of ylide which would be formed if k_q were zero. As long as the concentration of acrylonitriles is low enough such that $\tau_2 \gg \tau_1$, τ_2 can be accurately measured from the decay of the ylide absorption (see insert in Figure 2). Then the value of τ_1 is calculated from the time for the maximum absorption of 3, $t_{max} = \ln(\tau_2/\tau_1)\cdot(\tau_2\tau_1)/(\tau_2 - \tau_1)$ and/or by adjustment of the values of τ_1 and Y_m to get the best fit between the curves $[3]_t$ and OD_t vs time as shown in Figure 2. Measurements of $1/\tau_1$ and $1/\tau_2$ vs [olefin] are linear and give

$$k_c = 3.63 \pm 0.20 \times 10^7\ M^{-1}\ s^{-1} \text{ and } k_q = 2.06 \pm 0.02 \times 10^7\ M^{-1}\ s^{-1} \text{ for ACN}$$

$$k_c = 5.21 \pm 0.57 \times 10^8\ M^{-1}\ s^{-1} \text{ and } k_q = 1.60 \pm 0.15 \times 10^8\ M^{-1}\ s^{-1} \text{ for ClACN}$$

The rate of addition of 2 to alkenes with increasing π molecular electronegativity (TME, 3.0; HEX, 3.84; ACN, 5.36; ClACN, 5.46) exhibits a parabolic dependence, i.e., high reactivity toward both electron-rich and electron-poor alkenes. This behavior is similar to that of Ph–C–Cl in the presence of the same series of alkenes.[2d]

It is worth noting that independent measurements with time-resolved photoacoustic calorimetry[7] yielded the same slow rate ($k_i = 1.4 \times 10^6$ s^{-1} at 295 K in heptane) for the 1,2-H migration in methylchlorocarbene.

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Measurement of the Absolute Rate of 1,2-Hydrogen Migration in Benzylchlorocarbene

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A very common reaction of an alkylcarbene is the 1,2-migration of a hydrogen atom to produce an alkene.[5] Calculations[6-10] have deduced barriers to the rearrangement of singlet ethylidene ranging from 0 to 27 kcal mol^{-1} with the more recent ab initio methods favoring the smaller value. The intramolecular rearrangement has proven to be so rapid in simple singlet alkyl carbenes that it is impossible to intercept these species intermolecularly.

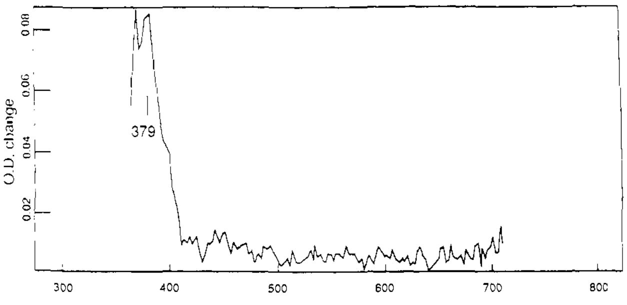
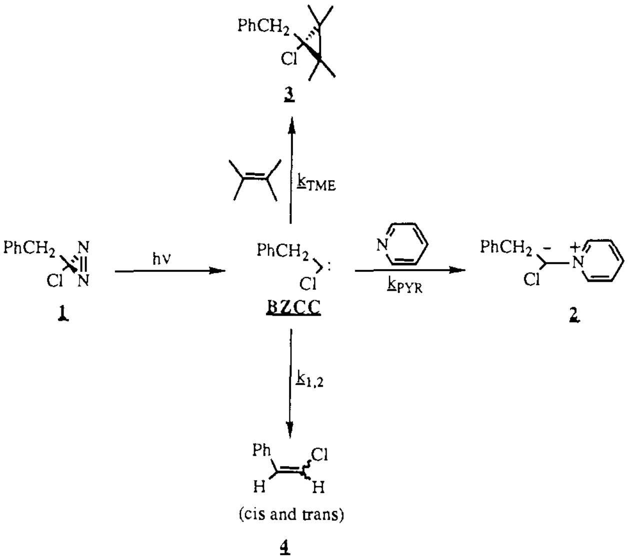


Figure 1. The transient spectrum of ylid **2** produced by laser flash photolysis of diazirine **1** in toluene containing pyridine solution.

Scheme I



Experimental work on 1-aryl-2-diazopropanes has produced evidence in favor of a barrier to 1,2-H-migration in dialkylcarbenes, but the barrier height was not estimated.[11] Recently, the products obtained from the thermolysis of 4-diazirinopentanoic acid[12] produced an estimate of 1.1 ± 1 kcal mol^{-1} for the barrier height ($\Delta H^{\ddagger}$) of the 1,2-H-shift in the corresponding dialkylcarbene.

The pioneering work of Moss and co-workers[13] has demonstrated that the presence of a halogen atom at a carbene center greatly stabilizes the singlet electronic state. This stabilization is sufficient to render the halo carbenes ground-state singlet species in contrast to methylene in which the triplet is the ground state.[14] The stabilization due to the chlorine substituent apparently retards the rate of the hydrogen shift reaction thereby enabling intermolecular reactions of the carbene to successfully compete with the intramolecular rearrangement.

Liu and Subramanian[15] have recently estimated the values of the barrier to rearrangement in benzylchlorocarbene by measuring

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(4) CNRS, Talence, France.

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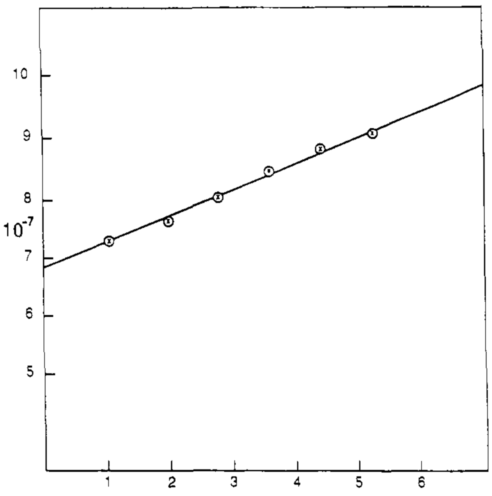

Figure 2. A plot of k_{obsd} describing the rate of formation of ylid **2** as a function of pyridine concentration. The slope is k_{PYR}, and the intercept is k_o (see text).

the ratio of cyclopropane **3** to styrene **4** obtained by photolysis of **1** in the presence of tetramethylethylene (TME) and assuming that k_{TME} for benzylchlorocarbene (BZCC) is similar to that of phenylchlorocarbene[16] with this olefin. Benzylbromocarbene was studied in an analogous fashion. The 1,2-hydrogen shift barriers ($\Delta H^{\ddagger}$) reported for $PhCH_2$–C–Cl and $PhCH_2$–C–Br were 6.4 and 4.7 kcal mol^{-1}, respectively. The estimated quantities may have errors of ±2 kcal mol^{-1}. We now wish to report the first absolute rate constant for 1,2-hydrogen migration in benzylchlorocarbene and the absolute rate constant for the reaction of this carbene with tetramethylethylene, butyl vinyl ether, and *trans*-3-hexene.

3-Chloro-3-benzyldiazirine, **1**, was prepared by Graham's method.[17] Laser flash photolysis[18] of **1** in isooctane in the presence of pyridine produces the transient spectra shown in Figure 1. This transient is not present in the absence of pyridine and is attributed to the ylid **2**. This spectrum is similar to the transient spectrum of the ylid derived from *tert*-butylchlorocarbene and pyridine.[19] A plot (Figure 2) of the observed pseudo-first-order rate constant (k_{obsd}, s^{-1}) for growth of ylid **2** against [pyridine] is linear. The slope of this plot yields the absolute rate constant for reaction of $PhCH_2$–C–Cl (BZCC) with pyridine, $k_{PYR} = 4.2 \pm 0.2 \times 10^9$ M^{-1} s^{-1}. Extrapolation of the data to zero [pyridine] yields an intercept equal to $6.7 \pm 0.2 \times 10^7$ s^{-1}. The intercept gives k_0 which is the sum of all intramolecular and pseudo-first-order decay channels of BZCC in the absence of pyridine. Photolysis[20] of **1** in the absence of pyridine or olefinic traps for the carbene results in a 73.4% yield of chlorostyrenes. Thus the rate of the 1,2-H atom shift in benzylchlorocarbene must be between 4.9 and 6.7×10^7 s^{-1}.

The absolute second-order rate constants of reaction of BZCC with various quenchers were obtained by monitoring the decrease in the maximum yield of the transient absorption of the ylid as a function of [quencher]. Stern–Volmer analysis produced absolute rate constants of BZCC with tetramethylethylene, *n*-butyl vinyl ether, and *trans*-3-hexene of 1.1×10^8, 7.2×10^7, and 6.8×10^7 M^{-1} s^{-1}, respectively.[21] These rate constants are comparable to the rate constants reported for the corresponding reactions of phenylchlorocarbene and *tert*-butylchlorocarbene with these olefins.[16,19] Methanol and methanol OD produced quenching plots with BZCC which exhibited severe curvature in a manner reminiscent of phenylchlorocarbene.[22] Studies of the temperature dependencies of these processes are in progress.[23]

Acknowledgment. We are indebted to Dr. J. C. Scaiano for his assistance with the LFP experiments in Ottawa and to the National Science Foundation (CHE-8513498) for support of this work.

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Kinetics of a Carbene Rearrangement: The 1,2-Carbon Migration of Cyclopropylchlorocarbene

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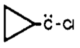
Direct observational kinetic studies of carbenes[2,3] have greatly augmented our understanding of their intermolecular chemistry,[3] but *directly observed intramolecular* kinetics have not yet been acquired for singlet carbenes in solution.[4,5] Cyclopropylchlorocarbene (**1**) exhibits competitive intramolecular (1,2-carbon migration to chlorocyclobutene (**2**) and intermolecular chemistry (addition to alkenes).[6] Here, we report that laser flash photolytic methods make possible direct determinations of the absolute rate constant for the **1** → **2** rearrangement, as well as rate constants for the additions of **1** to alkenes or pyridine. This is the first



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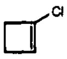

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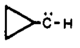

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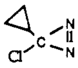

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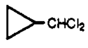

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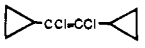

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