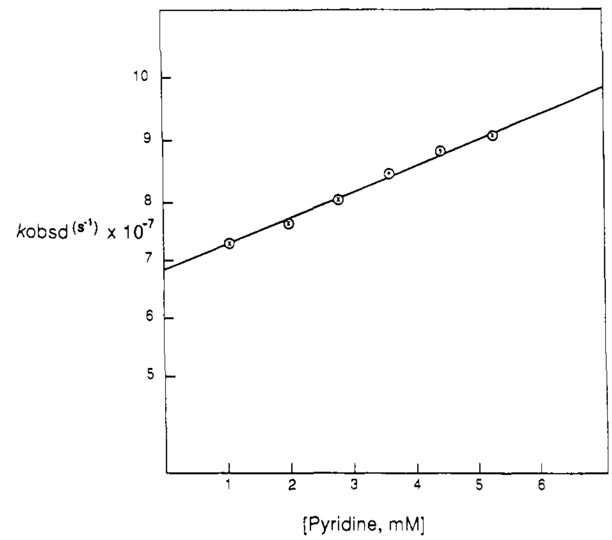

Figure 2. A plot of k_{obsd} describing the rate of formation of ylid **2** as a function of pyridine concentration. The slope is k_{PYR}, and the intercept is k_o (see text).

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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(17) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(18) The LFP set-up in Bordeaux uses a crossed-beams arrangement. The sample in a 10 × 10 mm cell is excited at 355 nm by single laser pulses (200 ps duration, 5–30 mj energy) provided by a frequency tripled mode-locked Nd-YAG (Quantel). The detection system includes a pulsed Xe-arc, a monochromator, a red-sensitive photomultiplier (Hamamatsu R446) and a fast transient recorder (Tektronix 7912) and has a response time around 5 ns.

(19) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.

(20) Photolysis of **1** in cyclohexane gives a 73.4% total yield of chlorostyrenes: Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1984**, 476.

(21) The data reported were measured in Columbus, ±50% error limits. A value of 8×10^8 M^{-1} s^{-1} for the reaction of BZCC with TME was determined in Bordeaux.

(22) Griller, D.; Liu, M. T. H.; Scaiano, J. C. **1982**, *104*, 5549.

(23) Ideally, it would be possible to confirm the predictions of the kinetic analysis by measuring the ratio of chlorostyrenes to cyclopropanes formed in the presence of a known quantity of TME. Unfortunately it has been shown that there are at least two precursors to chlorostyrene, one of which of course is not BZCC (Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Am. Chem. Soc.* **1984**, *106*, 454). One of us (M.T.H.L.) prefers to associate the second styrene forming intermediate with a reversibly formed BZCC–TME complex. Warner (Warner, P. M. *Tetrahedron Lett.* **1984**, *25*, 4211) has suggested that the second intermediate may be an excited state of BZCC. The workers in Columbus (J.E.J. N.S., M.S.P.) feel that there is a reasonable probability that **1** may photoisomerize to a diazo compound which can decompose to chlorostyrenes via ionic pathways.

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

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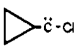
Direct observational kinetic studies of carbenes[2,3] have greatly augmented our understanding of their intermolecular chemistry,[3] but *directly observed intramolecular* kinetics have not yet been acquired for singlet carbenes in solution.[4,5] Cyclopropylchlorocarbene (**1**) exhibits competitive 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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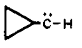

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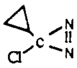

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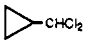

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(1) (a) Rutgers University. (b) University of Nevada-Reno.

(2) Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science* **1984**, *225*, 1439.

(3) Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15.

(4) For examples of H-migrations of triplet carbenes in very cold matrices, see: Platz, M. S. *Acc. Chem. Res.* **1988**, *21*, 236. McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683.

(5) The rate constant for 1,2-H migration in $PhCH_2CCl$ is ~7×10^7 s^{-1}, as determined from extrapolation of kinetic data for the competitive formation of the carbene's pyridinium ylide: Jackson, J. E.; Soundararajan, N.; White, W.; Liu, M. T. H.; Bonneau, R.; Platz, M. S. Submitted for publication. We thank Prof. Platz for permission to cite this work.

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0002-7863/89/1511-6875$01.50/0

absolute kinetic study of singlet carbene alkyl shifts, an important reaction channel for these species.[7] Additionally, we describe matrix spectrosocpy and chemistry of **1**, and pertinent theoretical studies. The matrix results are the first reported for a singlet alkylcarbene that is *not* stabilized by an oxy substituent,[8] and the computational work is of particular interest in view of two recent theoretical studies of the parent cyclopropylcarbene, **3**.[9]

3-Chloro-3-cyclopropyldiazirine[6,10] (**4**) was isolated in a nitrogen matrix (**4**;N_2 ~ 1:800) at 12 K and irradiated at 335 nm for 16 h, affording carbene **1**, with strongest IR absorptions at 1346, 921, 852, and 750 cm^{-1}, as well as product **2** and some fragmentation to ethylene and chloroacetylene.[11] Carbene **1** was photostable at 335 nm, but irradiation at 450 nm destroyed **1** in favor of the products. Photolysis of **4** in an argon matrix, doped (300;1) with HCl, gave IR signals due to **1** and small quantities of HCl-trapping product, **5**. Warming the matrix to 38 K caused rapid loss of the carbene bands, coupled with growth of the bands of **5**. Irradiation of **4** in a 3-methylpentane glass (335 nm, 40 K) gave **1** and product **2**, as well as some fragmentation. Warming the glass from 40 to 70 K caused the loss of the IR bands of **1** and formation of carbene dimer **6**. Only the dimer bands appeared to grow in this process.

Photolysis of diazirine **4** in the N_2 matrix at 14 K gave not only IR bands due to carbene **1** but also a broad visible absorption, centered at 460 nm ($\epsilon \sim 200$), and a more intense UV absorption at 240 nm ($\epsilon \sim 10^4$). Selective irradiation at either 435 or 240 nm caused the disappearance of *both* absorptions *and* also of the IR bands of **1**, confirming that the electronic absorptions belong to the carbene.

Steady state photolysis ($A_{348} \sim 1.0$, $\lambda > 350$ nm) of **4** in cyclohexane-d_{12} solution at 22 °C gave chlorocyclobutene **2**[6a] in ~75% absolute yield (NMR vs a decane standard). About 10% of the azine derived from diazirine **4** was present, and *possibly* ~12% of chloromethylenecyclopropane (δ 5.32), the 1,2-hydride shift product of **1**.[6a]

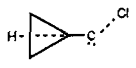
Irradiation at 20 °C of isooctane solutions of **4** ($A_{348} \sim 1.0$) with a 14-ns, 70–90-mJ, 351-nm pulse from a XeF excimer laser[12] afforded the low wavelength absorption of **1** (at 246 nm), previously observed in the matrix, although the carbene's weak visible absorption was not observed. The carbene transient absorption appeared within the laser pulse and (in isooctane or pentane) decayed with first-order kinetics at 250 nm, $k = 9.0 \pm 1.0 \times 10^5$ s^{-1} (10 repetitions). The decay is very largely attributable to the **1** → **2** rearrangement.

We thus assign $k_{1,2} \sim 9 \times 10^5$ s^{-1} to the 1,2-carbon shift of **1** to **2**. This assignment was supported in two ways. First, carbene **1** cyclopropanates trimethylethylene, *trans*-pentene, and acrylonitrile (in isooctane) competitively with its rearrangement to **2**. The observed rate constants for carbene decay at 250 nm increase linearly with [alkene], and the slopes of these correlations afford k_{add} for the bimolecular carbene/alkene additions.[13] From k_{add}, [alkene], and the capillary GC addition/rearrangement product ratio, one can calculate $k_{1,2}$.[14] For example, k_{add} for **1** and $Me_2C{=}CHMe$ was $6.0 \pm 1.0_2 \times 10^6$ M^{-1} s^{-1} at 20 °C. Conventional photolysis of **4** in 0.30 M alkene/isooctane gave P_2/P_{add}[14a] = $0.67 \pm 0.03_3$, from which $k_{1,2}^{calc} = 1.2 \pm 0.2 \times 10^6$ s^{-1}, in very good agreement with the observed $k_{1,2} = 9.0 \pm 1.0 \times 10^5$ s^{-1}. Analogous experiments with acrylonitrile and *trans*-pentene gave $k_{1,2}^{calc} = 4.8 \pm 0.7 \times 10^5$ and $6.9 \pm 1.0 \times 10^5$ s^{-1}, respectively.

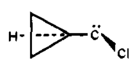
Second, laser flash photolysis of **4** in pyridine[15,16] (2–12 × 10^{-3} M in isooctane) gave a broad ylide absorption with $\lambda_{max} = 370$ nm. The observed rate constants for transient growth were linear with [pyridine], affording $k = 7.4 \times 10^8$ M^{-1} s^{-1} for ylide formation. The *Y*-intercept of this correlation at [pyridine] = 0 was 1.5×10^6 s^{-1}, in reasonable agreement with $k_{1,2} = 9 \times 10^5$ s^{-1} for unimolecular carbene decay.

Absolute rate constants for the addition of **1** to alkenes were determined by laser flash photolysis of **4** (in isooctane or pentane solutions at 20 °C) in the usual manner.[12-14b] The observed values (M^{-1} s^{-1}) were as follows: $Me_2C{=}CMe_2$ ($1.2 \pm 0.1_2 \times 10^7$), $MeCH{=}CMe_2$ ($6.0 \pm 1.0_2 \times 10^6$), *trans*-$MeCH{=}CHEt$ (4.9×10^5), $CH_2{=}CH$-*n*-Bu (7.4×10^4), $CH_2{=}CHCN$ ($4.1 \pm 0.5_2 \times 10^5$), and $CH_2{=}CClCN$ ($1.2 \pm 0.2_2 \times 10^8$). These rate constants are generally about an order of magnitude lower than those for the corresponding PhCCl additions,[17] and the observed *ambiphilic* selectivity pattern of **1** is both similar to that of PhCCl[17,18] and expected, based on the calculated differential frontier orbital energies for additions of **1** to these alkenes.[19]

Ab initio molecular orbital calculations help rationalize some of the properties of cyclopropylchlorocarbene.[20] Carbene **1** should exist as trans and cis ground-state singlets,[21] with *trans*-**1** computed 3.5 kcal/mol lower in free energy; $\Delta G^{\ddagger}$ for the cis → trans interconversion is 9.5 kcal/mol, This barrier governs the lowest energy reaction pathway for *cis*-**1** because its ring expansion to **2** requires $\Delta G^{\ddagger} = 25.2$ kcal/mol. In contrast, rearrangement of *trans*-**1** to **2** is only opposed by $\Delta G^{\ddagger} = 9.0$ kcal/mol and is strongly driven ($\Delta G_{rx} = -49.8$ kcal/mol).



trans - 1



cis - 1

We calculate frontier orbital energies for the σ(HOMO) and p(LUMO) orbitals of *trans*-**1** of −10.08 and 2.01 eV, respectively; the corresponding values for *cis*-**1** are −9.91 and 1.80 eV. Calculated alkene/carbene differential orbital energies[3] predict ambiphilic reactivity for either carbene conformer, but we are not certain whether both conformers, or only one, actually add to the olefins.[22]

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[8] Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Włostowski, M.; Kesselmayer, M. A.; Subramanian, R.; Kmiecik-Ławrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1988**, *110*, 7563.

[9] (a) Wang, R.; Deng, C. *Tetrahedron* **1988**, *44*, 7335. (b) Shevlin, P. B.; McKee, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 519.

[10] Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

[11] Products were identified by IR comparisons to authentic materials. A trace of cyclopropylchlorodiazomethane (2055 cm^{-1}) was produced. It was photolabile at $\lambda > 450$ nm, but is UV or visible absorptions could not be observed, presumably because of low concentration.

[12] Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Ławrynowicz, G.; Włostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341.

[13] Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7577.

[14] (a) $k_{1,2}^{calc} = k_{add}^{obsd}[alkene](P_2/P_{add})$, where P_2/P_{add} is the molar product ratio of **2** and the carbene/alkene adduct. (b) All new cyclopropanes were fully characterized, others were identical to prior preparations.[6a]

[15] Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.

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[18] 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.

[19] See ref 3 for a discussion of this method and below for calculated orbital energies of **1**.

[20] Calculations employed the GAUSSIAN 86 series of programs, Frisch, M. et al., Carnegie Mellon Publishing Unit, Pittsburgh, Pa. Computational methods included: HOMO-LUMO energies at HF/4-31G//3G (to conform with previous usage);[3] vibrational analysis at HF/3-21G//3-21G; single point calculations at HF/6-311G*//6-31G* and MP4(SDTQ)/6-31G*//6-31G*. Relative energies were combined: $\Delta E = \Delta E$(MP4(SDTQ)/(6-31G*//6-31G*) + ΔE(HF/6-311G*//6-31G*) - ΔE(HF/6-31G*//6-31G*) to simulate correlated energies with the 6-311G* basis set, and then converted to enthalpies using computed zero-point and thermal energies. $\Delta G = \Delta H - T\Delta S$, with computed ΔS and $T = 298$ K. Optical absorptions and intensities were computed with the semiempirical, all-valence electron INDO/S model with use of the HF/6-31G* geometries.

[21] Appropriate conformers of precursor **4** are isoenergetic (geometry optimized HF/3-21G calculations) to within 0.1 kcal/mol, so that both *cis*- and *trans*-**1** should be generated on photolysis of **4**.

[22] We are also uncertain whether one or both carbene conformers are present in the cold N_2 matrix. Thus, irradiation of matrix-isolated **1** at 405 or 495 nm (i.e., at either edge of its long wavelength absorption) caused uniform disappearance of *all* of its IR bands, consistent either with extensive overlap of the visible electronic bands of *cis*-**1** and *trans*-**1** or the presence of only one carbene conformer in the matrix.

We calculate[20] two electronic absorption bands above 200 nm for **1**: for *trans*-**1**, a weak $S_0 \rightarrow S_1$ ($\sigma^2 \rightarrow \sigma^1 p^1$) transition at 470 (oscillator strength, $f = 0.02$), and a much more intense $S_0 \rightarrow S_2$ ($\sigma^2 \rightarrow \sigma^1 \sigma_{C-Cl}{}^{*1}$) transition at 219 nm ($f = 0.09$). Corresponding *cis*-**1** transitions are calculated at 535 ($f = 0.01$) and 226 nm ($f = 0.07$). The calculated transitions and intensities are in good agreement with the observed weak and strong bands of matrix-isolated **1** at 460 and 240 nm, respectively, but only one long wavelength absorption was observed at low temperatures. The observed matrix IR bands of **1** are in reasonable agreement with the calculated[20] bands, but they do not clearly differentiate *cis*- and *trans*-**1**. These spectra will be discussed in detail in a separate publication.

The computed $\Delta G^{\ddagger}$ for the rearrangement of *trans*-**1** to **2** (9.0 kcal/mol) consists of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at 8.2 kcal/mol and −2.7 eu, respectively. A variable-temperature study of the rearrangment is in progress and will be reported in due course. Note, however, that the intricate "choreography" required for the concerted rearrangement of **3** to cyclobutene[9a] involves disrotatory motions of the migrating and carbenic carbons in different relative directions before and after the transition state. Should this carry over to the rearrangement of *trans*-**1** to **2**, then the free energy (variational) transition state might differ from the calculated (conventional) minimum energy transition state.[23]

Acknowledgment. We are grateful to the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society (R.S.S., K.K.-J.), and the A. P. Sloan Foundation (R.S.S.) for financial support. We thank Professor M. S. Platz for helpful discussions.

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The 1,2-Hydrogen-Shift Rearrangement in Alkylchlorocarbenes

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The 1,2-hydrogen-shift rearrangement of a singlet alkylcarbene to produce an olefin is a general reaction of current theoretical and experimental interest.[1] Although the rearrangement can be simply regarded as an insertion into an α C–H bond, the structure and energy of the transition state are still in question. Recent theoretical calculations predict this highly exothermic process to have an extremely low activation energy, ≤5 kcal/mol.[2] For example, the rearrangement of methylcarbene (CH_3CH) to ethylene is calculated to occur without thermal activation.[2a] However, experimental studies suggest that alkylchlorocarbenes may indeed have an appreciable lifetime in solution.[3-5] In fact, alkylchlorocarbenes undergo intermolecular cyclopropanation reactions with olefins in competition with the intramolecular hydrogen shift rearrangement.[5]

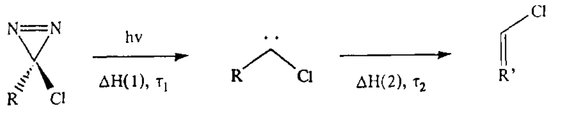
Table I. Enthalpic and Kinetic Parameters Determined by PAC for the Photochemical Reaction of **1** to **3**[a-c]

compd	$\Delta H(1)$, kcal/mol	$\Delta H(2)$, kcal/mol	τ_2, ns
1a	−27.5 (3.0)[d]	−42.1 (3.7)	740 (80)
1b	−61.9 (5.1)	n[e]	≤10
1c	−56.8 (3.4)	n[e]	≤10

[a] In heptane, 295 K, see ref 11–13 for experimental details. [b] Average of at least 5 measurements. [c] τ_1 is defined as ≤10 ns. [d] Values in parentheses are ±1σ. [e] Not resolved by PAC.

Unfortunately, no direct experimental kinetic data are currently available concerning the rearrangement of singlet alkylcarbenes. This may be due in part to the anticipated short lifetime of the reactive carbene and the difficulties in its direct spectroscopic detection.[6] In this regard, we wish to report the use of time-resolved photoacoustic calorimetry (PAC) to obtain both kinetic and thermodynamic data on the rearrangement of alkylchlorocarbenes. In particular, both the experimental heat of formation of methylchlorocarbene in solution and the effect of temperature on the rate constant for its 1,2 rearrangement to vinyl chloride are measured. These are among the first direct absolute rate constant measurements for such a process in solution.

Irradiation of the alkylchlorodiazirines (**1a–c**) initially produces alkylchlorocarbenes (**2a–c**) which subsequently undergo a 1,2-hydrogen shift to produce alkenyl chlorides (**3a–c**).[5,7]



1a $R = CH_3$
1b $R = CH_2CH_3$
1c $R = CH(CH_3)_2$

2a $R = CH_3$
2b $R = CH_2CH_3$
2c $R = CH(CH_3)_2$

3a $R' = CH_2$
3b $R' = CHCH_3$
3c $R' = C(CH_3)_2$

PAC allows for the simultaneous determination of the thermodynamic and kinetic properties of photogenerated reactive intermediates.[8-10] Deconvolution of the experimental acoustic waveforms measures the amplitude and time evolution of heat deposition. The details of this method have previously been reported.[8,9] The enthalpic and kinetic data for the photochemical reactions of **1a–c**, as determined by PAC, are given in Table I.[11-13]

Irradiation of **1a** in heptane results in two, time-resolved heat depositions. The first, $\Delta H(1)$, reflects carbene formation, **1a** → **2a**, and the second, $\Delta H(2)$, the unimolecular rearrangement, **2a** → **3a**. With use of $\Delta H(2)$ and the heat of formation of **3a**, 8.6 kcal/mol,[16a] the heat of formation of methylchlorocarbene,

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(11) The photoacoustic apparatus has been previously described.[8] Compounds **1a–c** and **1a**–d_3 are prepared by the Graham procedure[14] by using the appropriate acetonitrile precursor. 2-Hydroxybenzophenone is used as the calibration compound. Excitation is by nitrogen laser (337 nm) and detection employs a ~0.5 MHz transducer. Similar results are obtained in toluene or isooctane and are unaffected by sample concentration (0.2–0.8 OD) or argon degassing. The temperature (±0.1 °C) is controlled by Haake 80 bath.

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