8098 *J. Am. Chem. Soc.* **1996,** *118,* 8098−8101

Laser Flash Photolysis Studies on Intra- and Intermolecular Reactions of Some Halocarbenes

Michael T. H. Liu* and Roland Bonneau

Contribution from the Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, C1A 4P3 Canada, and URA 348, Laboratoire de Chimie Physique A, Université de Bordeaux I, 33405 Talence, France

Received January 18, 1996[⊗]

Abstract: Laser flash photolysis studies on α-methylbenzylchlorodiazirine, *n*-propylchlorodiazirine, and isopropylchlorodiazirine have been carried out at low temperatures, ranging from 170 to 230 K. The present results, together with those previously obtained with benzylchlorodiazirine and methylchlorodiazirine, provide a direct measurement of the "by-stander effect" of alkyl substituents on the C atom in the α position of the carbene center. Intermolecular reactions of α-methylbenzylchlorocarbene and tetramethylethylene in isooctane and methylcyclohexane have been measured but this reaction is shown to be too slow to measure by LFP in highly viscous decalin solvent.

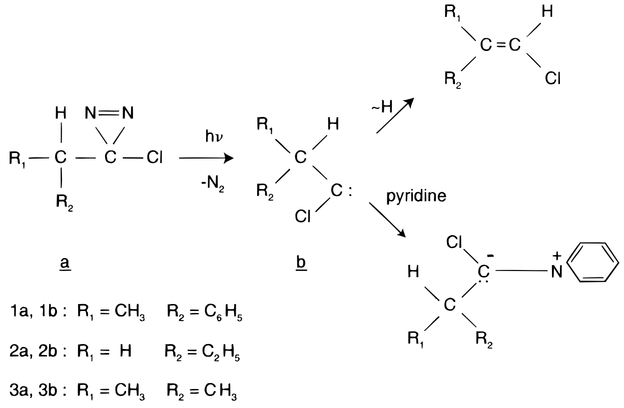
Introduction

In recent years, absolute kinetics of 1,2-H migration in many alkylhalocarbenes and dialkylcarbenes have been obtained by the laser flash photolysis (LFP) technique with rate constants ranging from 10^5 to 10^8 s^{-1}. Developments in this research area have been duly reviewed.[1] In 1989, we reported the rate constant for several alkylchlorocarbenes.[2] The lifetime of some carbenes was found to be too short at room temperature to be measured with our experimental apparatus which has a response time of approximately 4 ns. It should be possible to measure these lifetimes accurately at lower temperatures, because the 1,2-H migration usually shows a non-negligible activation energy. We now wish to report the results of LFP studies on α-methylbenzylchlorodiazirine (**1a**), *n*-propylchlorodiazirine (**2a**), and isopropylchlorodiazirine (**3a**). These results will be compared to those previously obtained with benzylchlorocarbene and methylchlorocarbene, thereby providing a direct measurement of the "by-stander effect" of alkyl substituants on the C atom in the α position of the carbene center, discussed by Nickon.[1b]

Experimental Section

Diazirines **1a**, **2a**, and **3a** were prepared by hypochlorite oxidation of the corresponding amidines.[3a] The decomposition products of **1a**, **2a**, and **3a** have been described previously.[3b,c] Tetramethylethylene was acquired from Aldrich and used without purification. Pyridine was distilled over CaH_2. The laser flash photolysis setup used a crossed-beam arrangement. The sample, in a 10 × 10 mm cell, was excited at 355 nm by single light pulses (200 ps; 5−30 mJ) provided by a frequency tripled mode-locked Nd-YAG laser (Quantel). The detection system (pulsed Xe arc, monochromator, photmultiplier, and Tektronix 7912 transient recorder) had a response time of approximately 4 ns. For low-temperature measurements, the cell holder was put in a clear Dewar flask, where it was cooled down to −120 °C by a stream of cold nitrogen gas. The temperature was measured with a thermocouple immersed in the solution, close to the region where the excitation and analytical beams cross each other.

Scheme 1



Results

In LFP experiments, every species that lacks a strongly absorbing chromophore, i.e., one with a molar absorption coefficient ≥10^3 M^{-1} cm^{-1}, is invisible to laser experiment with UV−vis detection. This difficulty was overcome by the pyridinium ylide probe technique developed by Jackson et al.[1f] The pyridinium probe technique may be used in two different ways, relying on the measurement of either the kinetics or the yield of the formation of the pyridinium ylide. In the Stern−Volmer method, the amplitude of the ylide absorption is measured as a function of pyridine, with excitation, temperature, and other variables being constant. The amplitude of the ylide absorption, OD, is proportional to $\Phi = k_y[\text{pyridine}]/(k_1 + k_y[\text{pyridine}])$. With P as the proportional factor, the yield is $OD = P\Phi$, and $1/OD = 1/P + k_1/Pk_y[\text{pyridine}]$. LFP of **1a**, in isooctane at 25 °C, in the presence of pyridine gives the pyridinium ylide absorption, at 370 nm. The plot of the reciprocal of the ylide absorption, 1/OD vs 1/[pyridine], yielded a straight line. The ratio slope/intercept of this line led to $k_1/k_y = 7.7 \times 10^{-2}$ M, where k_1 is the rate constant for disappearance of the α-methylbenzylchlorocarbene (**1b**), in the absence of

---

* Address correspondence to this author at the University of Prince Edward Island.

[⊗] Abstract published in *Advance ACS Abstracts*, July 1, 1996.

(1) (a) Schaefer, H. F. *Acc. Chem. Res.* **1979**, *12*, 288. (b) Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84. (c) Liu, M. T. H. *Acc. Chem. Res.* **1994**, *27*, 287. (d) Moss, R. A. *Advances in Carbene Chemistry;* Brinker, U., Ed.; JAI: Greenwich, CT, 1994; Vol. 1. (e) Moss, R. A. *Pure Appl. Chem.* **1995**, *67*, 741. (f) Jackson, J. E.; Platz, M. S. *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI: Greenwich, CT, 1994; Vol. 1.

(2) Bonneau, R.; Liu, M. T. H.; Rayez, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 5973.

(3) (a) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396. (b) Frey, H. M.; Liu, M. T. H. *J. Chem. Soc. A* **1970**, 1916. (c) Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Am. Chem. Soc.* **1984**, *106*, 454.

S0002-7863(96)00176-X CCC: $12.00

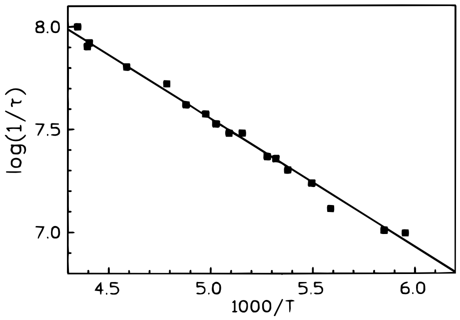


Figure 1. Arrhenius plot for 1,2-H shift in $C_6H_5(CH_3)CH{-}\ddot{C}{-}Cl$ obtained by measuring the rate of decay of carbene in isooctane at 305 nm.

Table 1. Temperature Dependence for $C_6H_5(CH_3)CH{-}\ddot{C}{-}Cl$ in Various Solvents

temp (°C)	τ(ns)	temp (°C)	τ(ns)	temp (°C)	τ(ns)
		Isooctane			
−43	10	−72	26.6	−87	50
−46	12	−74	29.8	−91	58
−45.5	12.5	−77	33	−94	77
−55	15.7	−79	33	−102	98
−64	19	−83	43	−105	101
−68	24	−85	44		
		Methylcyclohexane			
−68	27	−89	55	−106	120
−75	39.7	−93	67	−110	141
−76	37.4	−104	95	−116	185
−78	41	−105	91	−119	222
−88	48				
		Decalin			
−67	24	−88	55	−100	100
−74	30	−94	71	−101	102
−76	35	−95	80	−112	182
−78	35				

pyridine, and k_y is the rate constant for the reaction of **1b** with pyridine. Under the conditions that the reaction of **1b** with **1a** is not significant because the lifetime for **1b** is short and the concentration of **1a** is low, k_1 can be taken as the rate constant for the 1,2-H shift in **1b**. Assuming that $k_y \approx 7.5 \times 10^9$ M^{-1} s^{-1}, by similarity to the value measured with benzylchlorocarbene,[4] one gets $k_1 \approx 5.8 \times 10^8$ s^{-1}, i.e., a lifetime <2 ns for **1b** at 25 °C in the absence of pyridine, too short to be measured with our experimental setup.

In the absence of pyridine, at 230 K, LFP of diazirine **1a** in isooctane produces a transient species absorbing in the range of between 280 and 310 nm, assigned to **1b**, because of its similarity to benzylchlorocarbene.[4] The lifetime of this transient, monitored at 305 nm, is ≈10 ns at 230 K. This lifetime was measured as a function of temperature, from 170 to 230 K, in isooctane (Figure 1), methylcyclohexane (MCH), and decalin (mixture of cis and trans isomers). The results obtained in these solvents are similar (see Table 1). The corresponding Arrhenius plots are good straight lines yielding the following kinetic parameters:

$E_a = 2.85 \pm 0.06$, 2.46 ± 0.15, and 3.00 ± 0.06 kcal/mol and $\log(A) = 10.66 \pm 0.07$, 10.17 ± 0.18, and 10.80 ± 0.07 in isooctane, MCH, and decalin, respectively. The lifetime of **1b** was then measured as a function of temperature, in the same range (160−230 K) and in the same solvents, in the presence of tetramethylethylene (TME). Under these conditions, $1/\tau = k_1 + k_q[\mathrm{TME}]$ where k_q is the rate constant for reaction of **1b** with TME. In decalin (Figure 2) the carbene lifetime is not affected by the addition of TME up to 1 M, whereas it is substantially shortened in isooctane (Figure 3) with [TME] = 0.21 M and in MCH (Figure 4) with [TME] = 0.4 M. The value of k_q as a function of temperature was obtained by the difference between the reciprocal values of τ at various temperatures and the value of k_1 calculated at the same temperatures from the Arrhenius parameters listed above. This gives values of k_q around 7×10^7 M^{-1} s^{-1} in isooctane and 6×10^7 M^{-1} s^{-1} in MCH, but $<5 \times 10^6$ M^{-1} s^{-1} in decalin. These values of k_q are nearly independent of the temperature; the Arrhenius plots give "apparent activation energies" equal to 0.66 ± 0.10 kcal/mol in MCH and -0.17 ± 0.11 kcal/mol in isooctane with preexponential factors respectively equal to $(4.5 \pm 2.5) \times 10^8$ and $(5.5 \pm 3) \times 10^7$ M^{-1} s^{-1}.

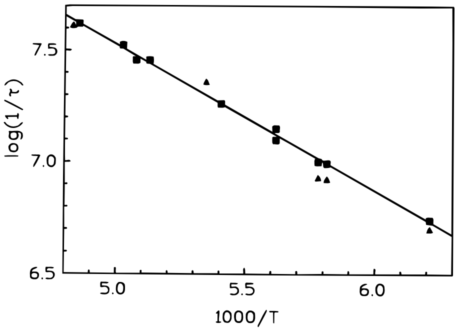


Figure 2. Arrhenius plot for $C_6H_5(CH_3)CH{-}\ddot{C}{-}Cl$ in decalin at 305 nm: ■, no TME; ▲, [TME] = 1.0 M.

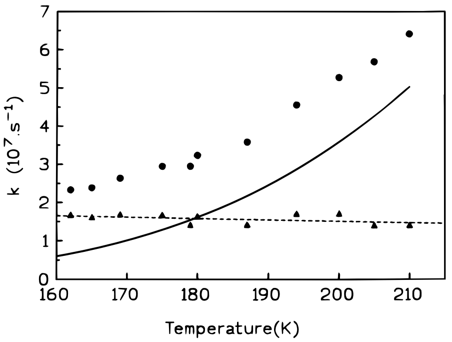


Figure 3. Quenching of $C_6H_5(CH_3)CH{-}\ddot{C}{-}Cl$ by TME in isooctane as a function of temperature: ●, $k_{obs} = k_1 + k_q[\mathrm{TME}]$. Solid line calculated from A and E_a in isooctane: ▲, $k_q[\mathrm{TME}]$ with [TME] = 0.21 M.

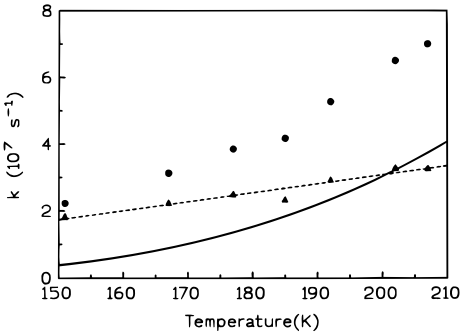


Figure 4. Quenching of $C_6H_5(CH_3)CH{-}\ddot{C}{-}Cl$ by TME in methylcyclohexane as a function of temperature: ●, $k_{obs} = k_1 + k_q[\mathrm{TME}]$. Solid line calculated from A and E_a in methylcyclohexane: ▲, $k_q[\mathrm{TME}]$ with [TME] = 0.4 M.

In the case of *n*-propylchlorodiazirine (**2a**), the LFP does not produce any observable transient which can be assigned to *n*-propylchlorocarbene (**2b**), but this "invisible" carbene may be studied by using the pyridinium ylide probe method.[1f] The kinetic analysis of the growth of the absorption of the pyridinium ylide, at 370 nm, gives $1/\tau_{growth} = k_{obs} = k_1 + k_y[\mathrm{pyridine}]$.

---

[4] Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1990**, *112*, 3915.

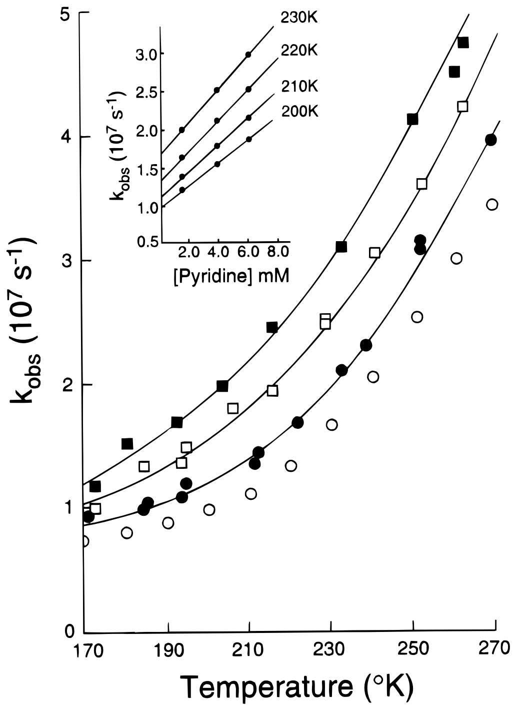


Figure 5. Plot of $1/\tau_{growth}$ or k_{obs} vs temperature in isooctane for three concentrations of pyridine (●, 1.55 mM; □, 4.0 mM; ■, 6.2 mM) obtained by measuring the growth of the pyridinium ylide at 370 nm. The bottom curve (○) gives the values of k_1 for 11 selected temperatures. INSET: Plot of k_{obs} vs [pyridine] with the slopes equal to k_y and intercepts equal to k_1.

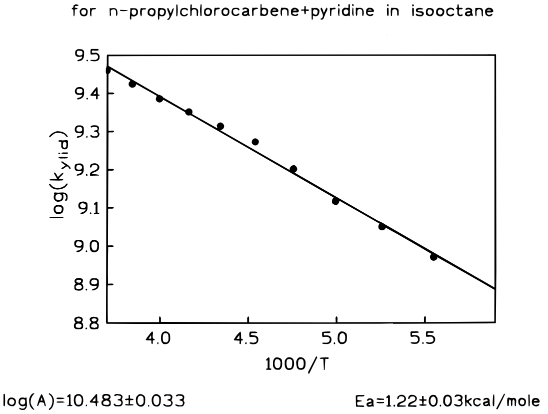


Figure 6. Arrhenius plot for the formation of pyridinium ylide by the reaction of *n*-propylchlorocarbene with pyridine.

The values of k_{obs} were therefore measured in isooctane, as a function of temperature from 170 to 270 K, for three concentrations of pyridine (1.55, 4.0, and 6.2 mM). Since the measurements were not made at the same temperatures for the three concentrations of pyridine, a smooth curve representing the variations of $1/\tau_{growth}$ vs T was drawn through each of the three sets of points (k_{obs}, T) corresponding to a given value of [pyridine] (see Figure 5). The values of $1/\tau_{growth}$ were then measured on these curves every 10 K, yielding the values of k_1 and k_y for 11 values of the temperature, ranging from 170 to 270K.

The Arrhenius plot (Figure 6) of log(k_y) vs $1/T$ is a good straight line and gives $\log_{10}(A) = 10.5$ and an apparent activation energy, $E_a(\text{meas}) = 1.22$ kcal/mol. In contrast, as shown on Figure 7, the plot of log(k_1) vs $1/T$ is approximately linear on the upper part of the temperature range but shows a pronounced curvature in the low-temperature region. This phenomenon, already observed for benzyl-[5] and methylchlorocarbene,[6] is due to a process with a low or a zero activation energy, which leads to the disappearance of the carbene, either by an intramolecular 1,2-H shift by tunneling[6] or by a reaction of the carbene with the solvent.[5] Assuming that the rate constant, k_x, of this enigmatic process, whatever its real nature may be, is equal to 7×10^6 s^{-1} over the whole temperature range considered here, the rate constant, k_i, of the "normal" 1,2-H migration in **2b** is given by $k_i = k_1 - k_x = (k_1 - 7 \times 10^6)$ s^{-1}. The plot of log(k_i) vs $1/T$ is then a good straight line, which gives the following kinetic parameters: log(A) = 10.44 ± 0.05 and $E_a = 3.64 \pm 0.05$ kcal/mol.

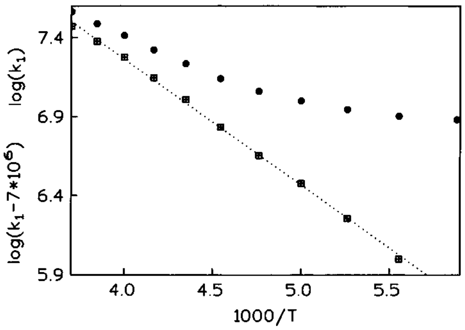


Figure 7. Plot of log(k_1) vs $1/T$ for **2b** in isooctane. The bottom line is log ($k_1 - 7 \times 10^6$) vs $1/T$.

The 1,2-H migration in the isopropylchlorocarbene (**3b**), produced by laser photolysis of **3a**, seems to be very fast, even at a low temperature, and no accurate measurement of the rate constant of this reaction could be made. The lifetime of **3b**, estimated from the kinetics of the growth of the pyridinium ylide absorption, is less than 20 ns at −90 °C. But this corresponds to τ_{growth}, which is close to the response time of our detection system because large amounts of pyridine have to be used. At low amounts of [pyridine], the low yield of conversion carbene ⇒ ylide (due to the short lifetime of carbene **3b**), coupled with the low yield of the production of the carbene upon photolysis of **3a** (previously noticed by Platz[7]), results in a small signal and a poor signal/noise ratio, so that τ_{growth} cannot be determined with accuracy even if τ_{growth}, at low temperature, would be long enough to be measurable.

Discussion

At room temperature, the above measurements yielded lifetimes of around 2 ns for **1b** and 17 ns for **2b**, to be compared respectively to 18 ns for benzylchlorocarbene[4] and 330 ns for methylchlorocarbene.[8] Since, in the absence of reactants, reaction pathways other than isomerization by 1,2-H migration are negligible, the reciprocal lifetime k_1 is equal to k_i. In both cases, the rate constant for 1,2-H migration, k_i, is strongly increased by alkyl substitution of the C atom in the α-position of the carbene center. This effect, named the "by-stander effect" by Nickon,[1b] is well-known. Whereas previous reports on this effect were founded on relative measurements of the rates of the rearrangement and addition reactions by products analysis, we now have a direct measurement of the enhancement of the rates of rearrangements. Clearly, this enhancement is not due to an increase of the frequency factor. The A factors measured in isooctane, $10^{10.44}$ s^{-1} for **2b** and $10^{10.66}$ s^{-1} for **1b**, are even slightly lower than the A factor measured for the benzylchlo-

---

(5) Liu, M. T. H.; Bonneau, R.; Wierlacher, S.; Sander, *W. J. Photochem. Photobiol. A: Chem.* **1994**, *84*, 133.

(6) (a) Dix, E. J.; Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 10424. (b) Storer, J. W.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 10426.

(7) White, W. R.; Platz, M. S. *J. Org. Chem.* **1992**, *57*, 2841.

(8) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1989**, *111*, 6873.

rocarbene, 10^{11} s^{-1}: in fact, the *A* factor is expected to be doubly smaller for **1b** than for benzylchlorocarbene because of the number of H on the C in the α position. The enhancement in rate constants is due to a decrease of the activation energy. For benzylchlorocarbene[5] E_a drops from 5.7 kcal/mol to 2.85, 2.46, or 3.00 kcal/mol (mean value, 2.77) upon substitution of one H by a methyl. Similarly, E_a changes from 4.9 kcal/mol in methylchlorocarbene[9] to 3.64 kcal/mol for **2b**.

In the case of **3b**, with the two methyl substituents on the α-C, the activation energy for rearrangement must be even lower, probably around 2 kcal/mol (this would give a 10-ns lifetime at −90 °C if the *A* factor is $10^{10.3}$, slightly lower than the *A* factor for **2b**). Therefore, lowering the temperature does not significantly increase the lifetime of **3b**.

When considering the rate constants of a bimolecular reaction, such as for the reaction of **1b** with TME, k_q, and for the formation of the pyridinium ylide of **2b**, k_y, diffusion must be taken into account. This explains why we could not detect any measurable decrease of the lifetime of **1b** upon addition of TME in decalin, a viscous solvent in the considered temperature range, since η increases from ≈1 *P* at 210 K to ≈100 *P* at 170 K.[10] The rate constant for diffusion is usually given at $k_{\text{diff}} = 8RT/3000\eta$, and the values of η as a function of *T* may be obtained from the literature.[10−12] The plots of $\log(T/\eta)$ vs $1/T$ are nearly straight lines in the range 210−170 K, yielding an "apparent activation energy" due to diffusion, E_a(diff), of around 2.6 and 3.4 kcal/mol in isooctane and MCH, respectively. Thus the activation energy of the reaction between **1b** and TME, E_a(react) $= E_a$(meas) $- E_a$(diff), would be $(-0.17 - 2.6) = -2.77$ in isooctane and $(0.66 - 3.4) = -2.74$ kcal/mol in MCH.

The correction term, E_a(diff), may be somewhat overestimated by this method. If the formation of the pyridinium ylide has virtually no activation energy, since the measured rate constants are close to a diffusion controlled limit, one would expect that E_a(meas) $= E_a$(diff) for this reaction. However, the values of E_a(meas) for the reaction of pyridine with **2b** and phenylchlorocarbene[13] in isooctane are 1.22 and 1.5 kcal/mol, respectively, significantly lower than the 2.6 kcal/mol obtained from the plot of $\log(T/\eta)$ vs $1/T$. Yet, even if the values of E_a(diff) obtained from the plots of $\log(T/\eta)$ vs $1/T$ were indeed overestimated by ≈1.4 kcal/mol, the values of E_a for the reaction between the **2b** and TME would still be negative, −1.35 kcal/mol in isooctane as well as in MCH. Negative values have already been reported for the activation energy of the reaction of phenylchlorocarbene[14] and benzylchlorocarbenes[15] with TME. They have been interpreted by the existence of a "carbene-olefin complex" (COC)[14,15] on the way to cyclopropanation or, alternatively, by a control of the reaction by entropic terms.[16] Theoretical chemistry[16] has denied the existence of a COC, as a minimum on the energy surface connecting the system "carbene + olefin" to "cyclopropane adduct".

During the last few years, there has been much controversy between those favoring one or the other of these interpretations.[1c,d,3] It still remains true that the analysis of products obtained by photolysis and thermolysis of diazirines[17] in the presence of olefins indicates an "excess" of rearrangement products, which can be explained only by a rearrangement occurring within a COC. The actual value of the probability for the COC to give cyclopropane instead of the rearrangement products depends not only on the diazirine but also on the olefin used as reactant. Steric factors as well as electron densities at the reactive centers on the carbene and the olefin may be decisive.

Acknowledgment. M. T. H. Liu thanks the NSERC of Canada for financial support.

JA960176U

---

[9] LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877.

[10] Von Salis, G. A.; Labhart H. *J. Phys. Chem.* **1968**, *72*, 752.

[11] Riddick J. A.; Bunger, W. *Tech. Chem. (N. Y.)* **1970**, *2*, 95.

[12] Murov, S. L. *Handbook of Photochemistry*; M. Dekker Inc., New York, 1973.

[13] Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Doyle, M. P.; Liu, M. T. H. *Tetrahedron Lett.* **1989**, *30*, 1335.

[14] Turro, N. J.; Lehr, G. F.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* **1982**, *104*, 1754.

[15] Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1992**, *114*, 3604.

[16] Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 4293.

[17] Bonneau, R.; Liu, M. T. H.; Kim, K. C.; Goodman, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 3829.