to N.J.B. and a postgraduate scholarship to S.R.C.

Registry No. DABCO, 280-57-9; 1-methoxy-4-nitronaphthalene, 4900-63-4; 1-fluoro-4-nitronaphthalene, 341-92-4; dimethylamine, 124-40-3; 1-(dimethylamino)-4-nitronaphthalene, 39139-76-9; 4-methoxy-1-naphthylamine, 16430-99-2; methylamine, 74-89-5; 1-(methylamino)-4-nitronaphthalene, 7000-88-6; 1-(diethylamino)-4-nitronaphthalene, 27210-64-6; diethylamine, 109-89-7; 4-methoxy-1-naphthalenecarbonitrile, 5961-55-7; *N*-methyl-*N*-(4'-methoxy-1'-naphthyl)-4-nitrobenzamide, 109392-85-0; isobutylamine, 78-81-9; propylamine, 107-10-8; aniline, 62-53-3; *N*-isobutyl-*N*-(4'-methoxy-1'-naphthyl)-4-nitrobenzamide, 109392-86-1; 1-(propylamino)-4-methoxynaphthalene, 109392-87-2; 1-nitro-4-pyrrolidinonaphthalene, 109392-88-3; 1-methoxy-4-pyrrolidinonaphthalene, 109432-29-3; 1-methoxy-4-piperidinonaphthalene, 109392-89-4; 1-nitro-4-piperidinonaphthalene, 34599-45-6; 4-piperidino-1-naphthylamine, 109432-30-6; pyrrolidine, 123-75-1; piperidine, 110-89-4; morpholine, 110-91-8; triethylamine, 121-44-8; diisopropylamine, 108-18-9; *tert*-butylamine, 75-64-9; KCN, 151-50-8.

Thermolysis and Photolysis of 3-Chloro-3-benzyldiazirines in Alkenes: Evidence for a Carbene–Alkene Complex

Michael T. H. Liu,* N. Soundararajan, N. Paike, and R. Subramanian

Department of Chemistry, University of Prince Edward Island, Charlottetown, P.E.I., C1A 4P3, Canada

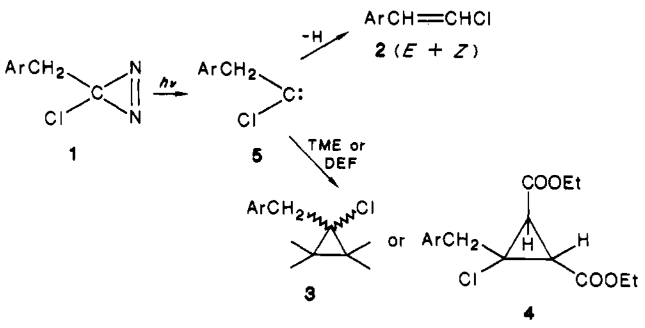
Received February 20, 1987

Photolysis and thermolysis of substituted 3-chloro-3-benzyldiazirines in alkenes yielded cyclopropanes and chlorostyrenes as products. The results suggest that the cyclopropanation of benzylchlorocarbenes is independent of substituents. However, 1,2-hydrogen migration is accelerated by OCH_3 or CH_3 substituents, and is decelerated by a Cl substituent on the phenyl ring. These results support the existence of an energy barrier to 1,2-H migration. Evidence is provided for carbene–alkene complexation.

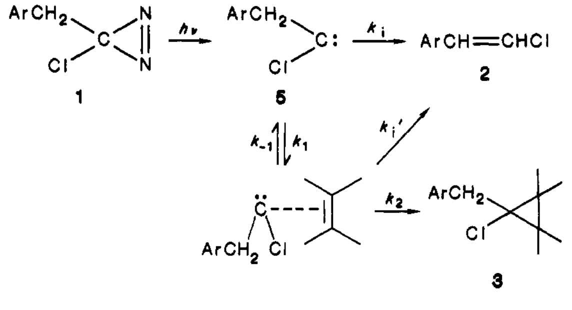
Time-resolved flash spectroscopic investigations[1,2] have shown that the reactions of singlet arylhalocarbenes with alkenes are consistent with the existence of transient carbene/alkene intermediates. Recent investigation on the additions of arylhalocarbenes to alkenes[3] suggest, however, that the observed negative activation energies could be explained in two ways. These results could be analyzed according to the Houk model.[4] Here, the carbene adds to the alkene in a single step, and the activation energy is entropic controlled. On the other hand, Turro and Moss[1,2] proposed a multistep model. In this case, the formation of a carbene–alkene complex could also be used to explain the results.

Our investigation shows that upon photolysis or thermolysis, 3-chloro-3-benzyldiazirine undergoes dinitrogen extrusion, and in the presence of alkene, the cyclopropanation directly competes with the intramolecular 1,2-hydrogen migration. The intervention of a reversibly[5-7] formed intermediate of carbene with alkene has also been advanced to rationalize the complex kinetic data for competitive carbene reactions. Giese and co-workers[8] have also suggested the general existence of intermediates in cyclopropanation reactions of singlet carbenes. The reactions of substituted benzylchlorocarbene with electron-rich (tetramethylethylene) and electron-poor (diethyl fumarate) alkenes were carried out to gain further insight into the 1,2-H migration and the cycloaddition of chlorocarbene. The results of the investigations are reported here.

Scheme I



Scheme II



Results and Discussion

3-Chloro-3-benzyldiazirines were synthesized by Graham's methods.[9] Irradiation of 3-chloro-3-benzyldiazirine at 4 K gives no detectable ESR signal.[6] The addition of benzylchlorocarbenes to alkene is stereospecific[5] which confirms that the carbenes are reacting as ground-state

---

[1] Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587.

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

[3] Moss, R. A.; Lawrynowicz, W.; Turro, N. J.; Gould, I. R.; Cha, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7028.

[4] (a) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291. (b) Houk, K. N.; Rondan, N. G. *Ibid.* **1984**, *106*, 4293. (c) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.

[5] Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Am. Chem. Soc.* **1984**, *106*, 454.

[6] (a) Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 982. (b) Liu, M. T. H.; Stevens, I. D. R. In *Chemistry of Diazirines*; Liu, M. T. H., Ed.; CRC: Boca Raton, FL, 1987; Chapter 5.

[7] Liu, M. T. H.; Subramanian, R. *Tetrahedron Lett.* **1985**, *26*, 3071.

[8] Giese, B.; Lee, W.-B.; Neumann, C. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 310.

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

[10] Liu, M. T. H.; Subramanian, R. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1233.

0022-3263/87/1952-4223$01.50/0

Table I. Product Distribution in the Thermolysis and Photolysis of 1b in TME

[TME], M	$h\nu$								Δ					
	20.4 °C		30.0 °C		40.4 °C		50.5 °C		80.2 °C		89.4 °C		99.5 °C	
	(*Z*)-**2b**/(*E*)-**2b**	**3b**/**2b**	(*Z*)-**2b**/(*E*)-**2b**	**3b**/**2b**	(*Z*)-**2b**/(*E*)-**2b**	**3b**/**2b**	(*Z*)-**2b**/(*E*)-**2b**	**3b**/**2b**	(*Z*)-**2b**/(*E*)-**2b**	**3b**/**2b**	(*Z*)-**2b**/(*E*)-**2b**	**3b**/**2b**	(*Z*)-**2b**/(*E*)-**2b**	**3b**/**2b**
0.10	0.19	0.525	0.18	0.372	0.18	0.249	0.19	0.171	0.12	0.0664	0.13	0.535	0.13	0.0380
0.15	0.20	0.722	0.19	0.530	0.19	0.363	0.19	0.248	0.12	0.106	0.13	0.0780	0.13	0.0583
0.20	0.22	0.916	0.20	0.664	0.20	0.463	0.20	0.341	0.12	0.142	0.13	0.0997	0.13	0.0781
0.30	0.24	1.21	0.22	0.920	0.22	0.648	0.21	0.457	0.13	0.206	0.13	0.152	0.14	0.115
0.40	0.26	1.46	0.24	1.12	0.23	0.805	0.22	0.568	0.13	0.259	0.13	0.212	0.14	0.123
0.60	0.29	1.80	0.27	1.43	0.25	1.07	0.24	0.773	0.13	0.359	0.14	0.313	0.14	0.235
1.00	0.35	2.22	0.31	1.77	0.29	1.37	0.27	1.04	0.13	0.542	0.14	0.439	0.14	0.350
1.50	0.36	2.39	0.34	2.03	0.32	1.61	0.30	1.27	0.13	0.751	0.14	0.608	0.14	0.494
k_i/k_t	0.162 ± 0.001		0.237 ± 0.002		0.365 ± 0.003		0.541 ± 0.009		1.44 ± 0.037		1.85 ± 0.028		2.59 ± 0.30	

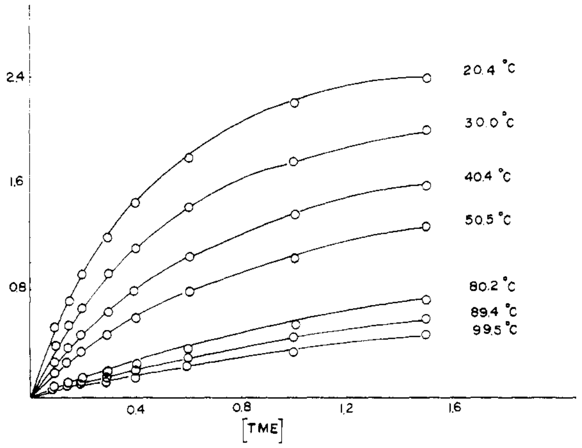


Figure 1. Plots of cyclopropane **3b**/chlorostyrene **2b** vs. [TME].

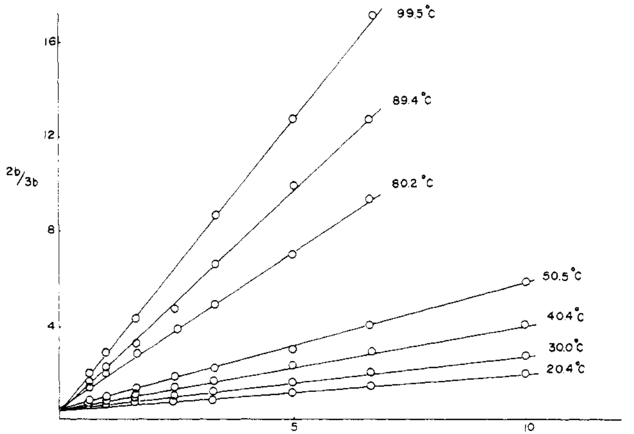


Figure 2. Plots of Chlorostyrene **2b**/cyclopropane **3b** vs. 1/[TME].

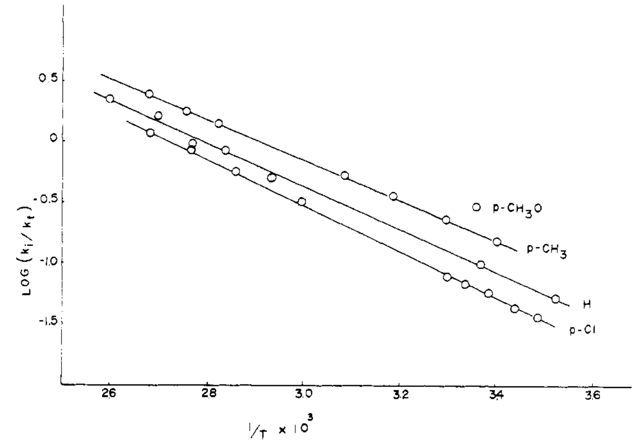


Figure 3. Arrhenius Plots for reactions of benzylchlorocarbenes with TME.

singlets. Photolysis of these diazirines (0.01 M) in the presence of excess alkene (TME or DEF) in isooctane gave (*E*)- and (*Z*)-β-chlorostyrenes and cyclopropanes by two competing reactions, as shown in Scheme I. The products of thermolysis in the case of TME were identical with those obtained in photolysis. The cyclopropane/chlorostyrenes product ratios were determined as a function of [TME] and temperature for the reaction of TME with 3-chloro-3-benzyldiazirine (**1a**), 3-chloro-3-(*p*-methylbenzyl)diazirine (**1b**), 3-chloro-3-(*p*-chlorobenzyl)diazirine (**1c**), and 3-chloro-3-(*p*-methoxybenzyl)diazirine (**1d**). However, in the presence of DEF as substrate, the cyclopropane/chlorostyrenes product ratios were recorded at only one temperature. The data are presented in Tables I–IV.

In general, plots of cyclopropane/chlorostyrenes product ratios vs. [TME] in photolysis exhibit pronounced curvature which suggests the formation of an intermediate prior to cyclopropane formation. However, thermolysis produced straight lines. Figure 1 shows representative plots for the reaction of diazirine **1b** with TME. Plots of **3b**/**2b** vs. [TME] go to the origin, indicating the absence of secondary reactions. This finding is confirmed by the fact that varying the diazirine concentrations from 0.01 to 1.0 M in excess TME left the measured [cyclopropane]/[chlorostyrene] ratios unchanged.

To account for the observed results, a mechanism is proposed (Scheme II) in which two parallel routes to the formation of β-chlorostyrene are operative. Application of steady-state treatment to the scheme leads to

$$[\text{complex}] = \frac{k_1[\text{TME}][\text{C:}]}{k_{-1} + k_i' + k_2} \tag{1}$$

Hence

$$\frac{\mathrm{d}[3]}{\mathrm{d}t} = \frac{k_1 k_2[\text{TME}][\text{C:}]}{k_{-1} + k_i' + k_2} \tag{2}$$

$$\frac{\mathrm{d}[2]}{\mathrm{d}t} = [\text{C:}]\left[k_i + \frac{k_i' k_1[\text{TME}]}{k_{-1} + k_i' + k_2}\right] \tag{3}$$

Combining eq 2 and 3 gives

$$\frac{2}{3} = \frac{k_i}{k_t}\,\frac{1}{[\text{TME}]} + \frac{k_i'}{k_2} \tag{4}$$

where the overall trapping rate constant, k_t, is equal to

$$k_1 k_2/(k_{-1} + k_i' + k_2)$$

According to eq 4, the ratio **2**/**3** has an inverse first-order dependence on TME. Figure 2 confirms this behavior. A least-squares analysis of the data in Table IV gives the

Table II. Product Distribution in the Thermolysis and Photolysis of 1c in TME

	hν												Δ					
	13.5 °C		18.0 °C		22.2 °C		26.3 °C		30.2 °C		60.2 °C		76.5 °C		87.4 °C		100.6 °C	
[TME], M	(Z)-2c/(E)-2c	3c/2c	(Z)-2c/(E)-2c	3c/2c	(Z)-2c/(E)-2c	3c/2c	(Z)-2c/(E)-2c	3c/2c	(Z)-2c/(E)-2c	3c/2c	(Z)-2c/(E)-2c	3c/2c	(Z)-2c/(E)-2c	3c/2c	(Z)-2c/(E)-2c	3c/2c	(Z)-2c/(E)-2c	3c/2c
0.10	0.27	1.54	0.27	1.37	0.26	1.18	0.26	1.04	0.24	0.943	0.21	0.284	0.13	0.172	0.14	0.110	0.16	0.085
0.15	0.31	1.89	0.32	1.73	0.30	1.54	0.29	1.37	0.28	1.23	0.23	0.413	0.13	0.257	0.14	0.170	0.15	0.141
0.20	0.33	2.03	0.33	1.87	0.32	1.71	0.31	1.58	0.30	1.42	0.24	0.513	0.13	0.329	0.14	0.216	0.16	0.170
0.30	0.37	2.26	0.37	2.25	0.36	2.07	0.34	1.90	0.34	1.74	0.26	0.714	0.14	0.493	0.15	0.340	0.16	0.245
0.40	0.38	2.49	0.40	2.45	0.38	2.29	0.37	2.11	0.36	2.03	0.27	0.870	0.14	0.597			0.16	0.327
0.60	0.40	2.68	0.42	2.75	0.41	2.51	0.40	2.38	0.39	2.24	0.30	1.08	0.14	0.854	0.15	0.587	0.16	0.435
1.00	0.46	3.36	0.45	3.14	0.47	3.12	0.48	2.69	0.47	2.44	0.35	1.37	0.19	1.22	0.17	0.946	0.22	0.745
1.5	0.49	3.44	0.54	3.23	0.46	3.26	0.52	2.81	0.49	2.66	0.38	1.56	0.18	1.78	0.19	1.13	0.21	1.04
k_i/k_t	0.0371 ± 0.003		0.0452 ± 0.002		0.0565 ± 0.002		0.0643 ± 0.001		0.0731 ± 0.001		0.308 ± 0.004		0.556 ± 0.005		0.878 ± 0.016		1.12 ± 0.033	

Table III. Product Distribution in the Photolysis of 1d in TME at 24 °C

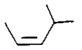
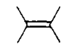
[TME], M	(Z)-2d/(E)-2d	3d/2d
0.25	0.22	0.507
0.50	0.26	0.696
0.75	0.23	0.807
1.00	0.23	0.904
1.25	0.26	0.950
1.50	0.34	1.10
1.75	0.29	0.935
2.00	0.30	1.02
2.25	0.34	1.04
2.50	0.33	1.13

k_i/k_t = 0.293 ± 0.0166

Table IV. Product Distribution in the Photolysis of Diazirines 1c and 1d in DEF at 17.5 °C

[DEF], M	(Z)-2c/(E)-2c	4c/2c	(Z)-2d/(E)-2d	4d/2d
0.1	0.60	0.217	0.11	0.0737
0.15	0.59	0.316	0.12	0.104
0.2	0.62	0.393	0.13	0.130
0.3	0.67	0.474	0.13	0.136
0.4	0.74	0.471	0.14	0.153
0.6	0.82	0.493	0.18	0.156
k_i/k_t	0.315 ± 0.041		0.918 ± 0.089	

Table V. k_i/k_t Values for $XC_6H_4CH_2\ddot{C}Cl$ with Various Substrates

	substrates			
X	CH₃OH (25 °C)[10]	 (10 °C)[5]	 (24 °C)	DEF (17.5 °C)
CH_3O (**4d**)	0.417	0.557	0.293	0.918
CH_3 (**4b**)	0.148	0.298	0.205	
H (**4a**)	0.0921	0.167	0.0966[6]	0.460[7]
Cl (**4c**)	0.0817	0.132	0.0635	0.315

k_i/k_t values, with error limits quoted as the standard deviations. A plot of log (k_i/k_t) vs. $1/T$ for **1a–d** in TME is shown in Figure 3.

Both the thermolysis and photolysis data fall on the same straight line when applied to an Arrhenius plot. This suggests similar reactions in thermolysis and photolysis. Had the equation $k_t = k_1k_2/(k_{-1} + k_i' + k_2)$ not been reduced to k_1k_2/k_{-1} or Kk_2, the Arrhenius law could not have applied. In order to achieve this limiting condition, k_{-1} must be greater than k_2 or k_i'. Turro and Moss[2] have shown in the laser photolysis of 3-chloro-3-phenyldiazirine in TME, that $k_{-1} \gg k_2$ at room temperature. As well, the values for k_i'/k_2 derived from the intercepts in Figure 2 are approximately equal to 0.3. This satisfies the second condition, $k_i' \simeq k_2$.

On the basis of the slopes in Figure 3, values for $E_i - E_t$ were evaluated: (**5a**) 8.10 ± 0.2, (**5b**) 7.6 ± 0.1, and (**5c**) 8.7 ± 0.1 kcal mol.$^{-1}$ From the intercepts, the values for $\Delta S_i^\ddagger - \Delta S_t^\ddagger$ were obtained: (**5a**) 24.4, (**5b**) 24.2, and (**5c**) 25.8 cal K^{-1} mol^{-1}. Since $\Delta S_i^\ddagger$(**5a**)[6] is −4.5 cal^{-1} K^{-1} mol^{-1} ($A = 10^{12.2}$) at 298 K, $\Delta S_t^\ddagger$ for **5a–c** will be largely negative. This is consistent with cycloaddition reactions.

The decreasing values of k_i/k_t in the order of p-MeO > p-Me > H > p-Cl (Table V) reflect the effects of substituents in the aryl group. The Hammett plot (Figure 4) for log (k_i/k_t) vs. σ^+ values[11] gave ρ values of −0.80, −0.70, −0.72, and −0.47 in methanol, (Z)-4-methyl-2-pentene, TME, and DEF, respectively. The similarity in reaction constant for benzylchlorocarbene reaction with the above substrates suggests that the addition reactions to form

---

[11] March, J. *Advanced Organic Chemistry*, Wiley-Interscience: New York, 1985; p 244.

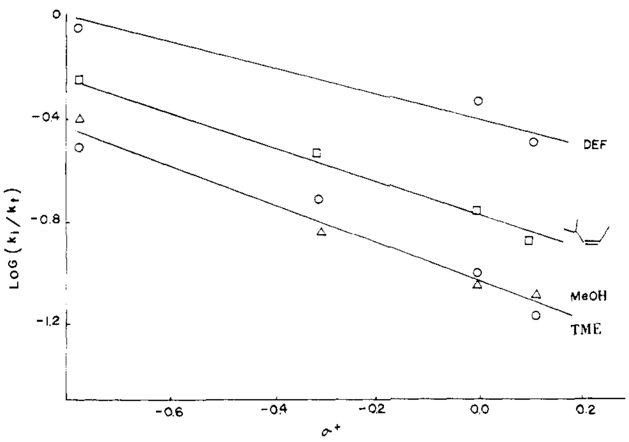
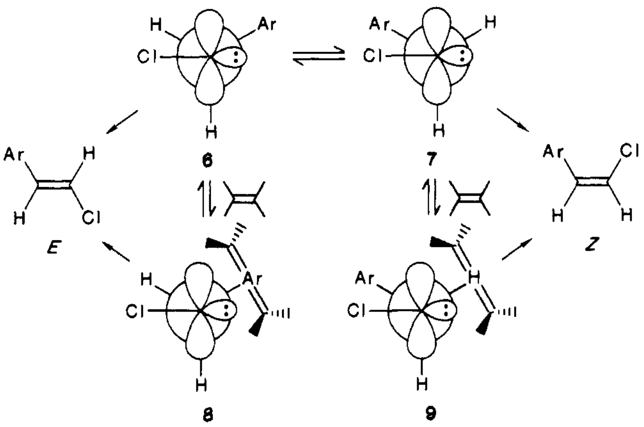


Figure 4. Hammett plots for log (k_i/k_t) vs. σ^+.

Scheme III



cyclopropanes or acetal are more or less independent of the substituents. This is a reasonable assumption, because the substituents do not directly conjugate with the carbenic center. The negative ρ values in these cases can, therefore, be attributed primarily to the substituent effects on the 1,2-H migration of benzylchlorocarbene. 1,2-Hydrogen migration is accelerated by methoxy or methyl substituents and is decelerated by a chloro substituent on the phenyl ring. Electron-donating groups better stabilize the δ^+ charge developed in the transition state, and confirm the hydride-like character of the 1,2-H shift to the carbenic center. This also supports the existence of an activation barrier to 1,2-H migration, which contradicts the prevailing view that migrations of this type can occur with zero activation energies.[12] If the activation energies (E_t) for cyclopropanation (X-Bz-$\ddot{C}$-Cl + TME) are similar, and if the activation energy for Bz-$\ddot{C}$-Cl + TME is taken to be the same[13] as Ph-$\ddot{C}$-Cl + TME (-1.7 kcal mol^{-1}),[2] then the activation barriers for 1,2-H migration (E_i) in substituted benzylchlorocarbenes will be (CH_3) 5.9, (H) 6.4, and (Cl) 7.0 kcal mol^{-1}. The substituent effects observed here are in broad agreement with MNDO investigation of the 1,2-rearrangement of singlet carbenes.[14] For a given carbene, the difference in k_i/k_t (Table V or Figure 4) reflects the relative rates of addition to various olefins. Thus, the rates for benzylchlorocarbene cyclopropanation are as follows: TME > (*Z*)-4-methyl-2-pentene > DEF.

Table VI. Low-Temperature Photolysis of Diazirine 1a in TME/Benzene Matrix[a]

[TME], M	(*Z*)-**2a**/(*E*)-**2a** (-196 °C)	(*Z*)-**2a**/(*E*)-**2a** (-210 °C)
0.11	1.1	1.1
0.30	1.2	1.2
0.60	1.2	1.2
1.03	1.2	1.1
1.94	1.2	1.1

[a] Yield of cyclopropane is ~3% at these temperatures.

The stereochemistry result of the (*Z*)/(*E*)-chlorostyrenes in Tables I-IV is of particular interest. In general, the (*Z*)/(*E*)-**2** ratios increase with increasing TME concentrations. In DEF, the process is similar but to a lesser degree. 1,2-Hydrogen migration occurs through the two limiting conformers **6** and **7** (Scheme III). (*E*)-β-Chlorostyrene arises from **6**, and the *Z* isomer is formed from **7**. As a result of olefin repulsion by the aryl group, **9** is expected to be more stable than **8**. This explanation accounts for the increase in *Z* with increasing olefin concentration. The depictions of **8** and **9** are not meant to imply a specific π complex. Rather, they represent a spectrum of intermediates, whose precise formulation depends on the carbene and olefin.

Revealing information was obtained when diazirine **1a** was photolyzed in TME at -196 and -210 °C (Table VI). At these temperatures, the cyclopropane formation was ~3% of the total product and the *Z*/*E* ratio of **2** was invariant with TME concentration.

Kinetic analysis on Scheme III gives

$$\frac{Z}{E} = \frac{k_7 + k_9[\mathrm{TME}]}{k_6 + k_8[\mathrm{TME}]}$$

where k_6 = rate constant for H shift from **6** to *E*, k_7 = rate constant for H shift from **7** to *Z*, and k_8 and k_9 are complex ratio of individual *k*'s involving the carbene-alkene complex. At a temperature (100 °C) where the formation of cyclopropane is not favored, $k_7 > k_9$ and $k_6 > k_8$, *Z*/*E* will be independent of [TME]. At intermediate temperatures, where $k_7 \simeq k_9$, the *Z*/*E* ratio will be [TME] dependent as observed. In the -196 and -210 °C matrix reactions, where little cyclopropane is formed, $k_7 > k_9$, and the *Z*/*E* ratio again became independent of [TME]. Furthermore, the *Z*/*E* ratio has increased to 1.1 as the reaction phase changed from liquid to solid. Due to limited diffusibility in a matrix environment, the leaving N_2 is forced to remain in the vicinity of the carbene. The steric repulsion of N_2 and the aryl group is greatest in **6**. Thus, conformer **7** is favored, leading to a higher concentration of (*Z*)-chlorostyrene.

These results clearly demonstrate the involvement of TME in the formation of chlorostyrene at the intermediate temperatures. The *Z*/*E* ratio will increase with increasing alkene concentration as long as sufficient cyclopropane is formed. Therefore, the *Z*/*E* ratio can be used to monitor carbene-alkene complexation. This suggestion is further corroborated by the work of Tomioka and Liu[15] in which (α-methylbenzyl)chlorodiazirine was photolyzed in (*Z*)-4-methyl-2-pentene. The methyl substituent on the α-carbon enhances the 1,2-H shift in $PhCH(CH_3)\ddot{C}Cl$ by two orders of magnitude, compared with $PhCH_2\ddot{C}Cl$. Only small amounts of cyclopropane is formed even with 500-

---

[12] Schaefer, H. F., III. *Acc. Chem. Res.* **1979**, *12*, 288.

[13] Similar methodology was used in ref 6 to estimate E_i for Bz-C-Cl (6.4 kcal mol^{-1}). The E_i thus obtained was used in ref 7 to estimate the E_t for Bz-C-Cl + DEF (0.1 kcal mol^{-1}). The activation energy by laser spectroscopy for Ph-C-Cl + DEF in toluene and is of the order of 1.1 kcal mol^{-1} (Soundararajan, N.; Liu, M. T. H.; Jackson, J. E.; Platz, M. S., unpublished results). The error involved in our assumption is less than 2 kcal mol^{-1}.

[14] Frenking, G.; Schmidt, J. *Tetrahedron* **1984**, *40*, 2123.

[15] Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1984**, 476.

Table VII. ^{1}H NMR Spectra of Cyclopropanes 3 and 4

	overall yield, %	^{1}H NMR spectra, δ
3a	90	1.13 (s, 6 H, CH_3), 1.25 (s, 6 H, CH_3), 3.18 (s, 2 H, CH_2), 7.18 (s, 5 H, Ar H)
3b	92	1.14 (s, 6 H, CH_3), 1.24 (s, 6 H, CH_3), 2.31 (s, 3 H, Ar CH_3), 3.12 (s, 2 H, CH_2), 7.00 (s, 5 H, Ar H)
3c	89	1.12 (s, 6 H, CH_3), 1.24 (s, 6 H, CH_3), 3.12 (s, 2 H, CH_2), 7.10 (s, 4 H, Ar H)
3d	90	1.16 (s, 6 H, CH_3), 1.28 (s, 6 H, CH_3), 3.16 (s, 2 H, CH_2), 3.82 (s, 3 H, Ar OCH_3), 6.8–7.4 (m, 4 H, Ar H)
4a	60[a]	1.25 (t, J = 6 Hz, 6 H, ester CH_3), 2.81 (m, 2 H, benzyl CH_2), 3.30 (s, 2 H, cyclopropane H), 4.20 (q, J = 6 Hz, 4 H, ester CH_2), 7.26 (s, 5 H, Ar H)
4c	72[a]	1.22 (t, J = 6 Hz, 6 H, ester CH_3), 2.80 (m, 2 H, benzyl CH_2), 3.32 (s, 2 H, cyclopropane H), 4.20 (q, J = 6 Hz, 4 H, ester CH_2), 7.20 (br s, 5 H, Ar H)
4d	62[a]	1.26 (t, J = 6 Hz, 6 H, ester CH_3), 2.82 (m, 2 H, benzyl CH_2), 3.32 (s, 2 H, cyclopropane H), 3.78 (s, 3 H, Ar OCH_3), 6.8–7.4 (m, 4 H, Ar H)

[a] The low material balance in these cases is due to the presence of some unidentifiable components in the GC analyses other than the chlorostyrenes and cyclopropanes.

fold excess of alkene. The Z/E ratio of the chlorostyrene remains unchanged. This is the only benzylchlorocarbene reacting with electron-rich alkene at room temperature where the Z/E ratio of chlorostyrene is independent of alkene concentration.

We will note in general that the ratio **3**/**2** is approaching saturation when the alkene concentration exceeds 1.0 M. The diazirine concentration (0.01 M) is very small when compared to the concentration of the alkene. This may suggest that the carbene reactions occur in-cage, but it would be inappropriate to speculate on this topic without further studies.

Experimental Section

The NMR spectra have been recorded on a Varian T-60 spectrometer. GLC analyses of absolute yields of products were performed on a Varian Vista 6000 gas chromatograph fitted with a 6 ft × 0.125 in. stainless steel column packed with CSP-20M and by using a flame ionization detector. The GC traces were calibrated by using authentic samples of the reaction products in each case. Peak areas were integrated with a Hewlett-Packard 3390A recorder.

Irradiation was carried out with 3500 UV lamps in a Rayonet photoreactor until all the diazirine (0.01 M in isooctane solution) was destroyed. Temperature control was within ±0.1 °C. The temperature of −210 °C was achieved by using solid nitrogen. 3-Chloro-3-benzyldiazirines were prepared by Graham's method[9] and purified by chromatography on silica gel. All diazirines were stable, and the absence of chlorostyrenes prior to photolysis or thermolysis was confirmed by NMR spectroscopy.

Product Studies: Photolysis of 3-Chloro-3-benzyldiazirines (1) in TME. 3-Chloro-3-benzyldiazirine (3×10^{-3} mol) and TME (3×10^{-2} mol) were dissolved in dry isooctane (25 mL), and the solution was photolyzed for 48 h at 15 °C. The unreacted TME and solvent were distilled off under reduced pressure. The chlorostyrene and cyclopropane were analyzed by G. C. The residue was chromatographed on a column of silica gel (25 mm × 300 mm) and eluted with hexane containing 1–5% of ethyl acetate. In every instance, the chlorostyrenes **2** were eluted in the first 200 mL of the solvent, and the subsequent fractions contained the cyclopropanes **3**. The chlorostyrenes were identified by comparison of their NMR spectra with those of authentic samples.[16] The cyclopropanes were characterized by means of NMR and mass spectral analysis. Authentic samples of **2** and **3** were used to calibrate the GC, and the absolute yields of **2** and **3** were determined from the integrated areas of the components in the GC analysis. Table VII gives the overall yield of the reaction based on **1** used along with the NMR spectra of the cyclopropanes **3**.

Product Studies: Photolysis of 3-Chloro-3-benzyldiazirines (1) in DEF. 3-Chloro-3-benzyldiazirine (3×10^{-3} mol) and DEF (3×10^{-2} mol) were dissolved in dry isooctane (25 mL), and the solution was photolyzed for 48 h at 15 °C. The solvent was distilled under reduced pressure on a water bath, and the unreacted DEF present in the residue was distilled by using a Kugelrohr apparatus under vacuum (0.05 mmHg) below 50 °C. The residue was chromatographed over silica gel in hexane to furnish the cyclopropanes **4**. Yields of the chlorostyrenes **2** and cyclopropanes **4** were calculated from the integrated areas of the components in the GC analysis of the residues before the Kugelrohr distillation. Table VII gives the overall yield of the reaction based on **1**, used along with the NMR spectra of the cyclopropanes **4**.

Acknowledgment. M.T.H.L. thanks NSERC of Canada for financial support and Professor M. P. Doyle for helpful discussion. We thank W. Kwan and A. Trainor for technical help.

Registry No. 1a, 88211-05-6; **1b**, 93746-79-3; **1c**, 91309-66-9; **1d**, 91309-65-8; (Z)-**2b**, 18684-80-5; (E)-**2b**, 18684-95-2; (Z)-**2c**, 18684-82-7; (E)-**2c**, 18684-97-4; (Z)-**2d**, 18684-79-2; (E)-**2d**, 18684-94-1; **3a**, 97073-41-1; **3b**, 109890-32-6; **3c**, 109890-33-7; **3d**, 109890-35-9; **4a**, 109890-31-5; **4c**, 109890-34-8; **4d**, 109890-36-0; tetramethylethylene, 563-79-1; diethyl fumarate, 623-91-6.

---

[16] Dolby, L. J.; Wilkins, C.; Frey, T. G. *J. Org. Chem.* **1966**, *31*, 110.