(3 mL) [freshly distilled over sodium sulfate and BSA] were added at room temperature allyl bromide (0.24 g, 0.17 mL, 2.0 mmol) and cesium carbonate (0.46 g, 1.4 mmol). The solution was heated to reflux for 3 h, cooled, and poured into a mixture of ice water and ether. The organic phase was separated and the aqueous phase was extracted with ether (3×). The combined organic phase was washed with brine and dried over magnesium sulfate. The solvent was removed in vacuo and the crude material was purified by column chromatography [silica gel, hexane/ether (6/1)] to afford 0.24 g (97%) of the title compound: IR (neat) 2944, 1942, 1736, 1640, 1433, 1215, 1112, 818 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.51 (m, 2 H), 7.35 (m, 3 H), 5.62 (ddt, J = 17, 10, 6 Hz, 1 H), 5.08 (d, J = 17 Hz, 1 H), 5.05 (m, 2 H), 4.63 (q, J = 7.5 Hz, 1 H), 3.68 (s, 6 H), 2.66 (d, J = 7.5 Hz, 2 H), 2.60 (dd, J = 7.5, 3 Hz, 2 H), 0.33 (s, 6 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 211.68, 171.14, 171.07, 138.18, 133.60, 132.29, 129.17, 127.80, 119.21, 80.98, 77.67, 57.97, 52.39, 52.33, 36.70, 31.54, −2.36; exact mass calcd for $C_{20}H_{26}O_4Si$ 358.1601, found 358.1597.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their generous support of our programs. J.M.T. thanks the National Institutes of Health for a postdoctoral fellowship for a portion of his stay in these laboratories. Mass spectra were gratefully provided by the Mass Spectrometry Facility, University of California–San Francisco, supported by the NIH Division of Research Resources.

Registry No. 1 (n = 1), 117687-47-5; 2 (X = OH), 117687-48-6; 11, 18042-55-2; 12, 117687-50-0; BSA, 10416-59-8; PhMe$_2$SiLi, 3839-31-4; ClAlEt$_2$, 96-10-6; PhMe$_2$SiCl, 768-33-2; PhMe$_2$SiCH=C=CHCH$_2$OCO$_2$CH$_3$, 117687-49-7; MeO$_2$CCH$_2$CO$_2$Me, 108-59-8; allyl bromide, 106-95-6; epoxybutyne, 6924-81-8.

Studies on Benzylchlorocarbene

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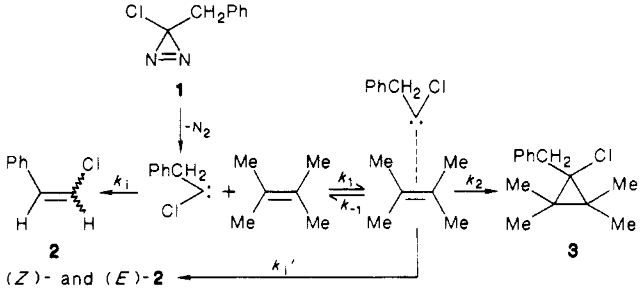
Photolysis or thermolysis of 3-chloro-3-benzyldiazirine (1) undergoes dinitrogen extrusion and in the presence of alkene, cyclopropanation directly competes with the intramolecular 1,2-hydrogen migration.[1,2] The intervention of a reversibly formed carbene–alkene complex, based on the Turro–Moss model,[3] has been advanced to rationalize the kinetic data for competitive carbene reactions.

Laser flash photolysis (LFP) indicates that increasing solvent polarity has no significant influence on the rates of carbene–alkene cycloaddition.[3,4] Here we report the results of our investigation on the solvent-induced effect of such a carbenic process, which involves a competing intramolecular rearrangement. Also, though it is well known[5,6] that 1,2-H migration in a carbene results in a mixture of isomeric olefins, the energetics of the equilibrium between the carbene conformers is hitherto not known. Here we determine if the isomeric olefins produced from the thermal decomposition of diazirine 1 are in thermodynamic quantity.

Scheme I



Results and Discussion

3-Chloro-3-benzyldiazirine (1) was synthesized by Graham's method[7] and 0.02 M solutions of 1 in the presence of excess tetramethylethylene (TME) in acetonitrile were photolyzed and thermolyzed over the 20–95 °C temperature range. The cyclopropane 3/chlorostyrene 2 product ratios as well as the Z/E ratios of 2 are given in Table I. A mechanistic model (Scheme I) accounts not only for the curvature in 3/2 vs [TME] plots but also predicts the change in Z/E ratio of 2 with increasing TME concentration. Application of steady-state treatment to the scheme leads to eq 1. Values for k_i/k_t were obtained by

$$\frac{2}{3} = \frac{k_i}{k_t} \times \frac{1}{[\mathrm{TME}]} + \frac{k_i'}{k_2} \tag{1}$$

correlating 2/3 vs 1/[TME] where k_t is equal to k_1k_2/k_{-1}. Plots of log k_i/k_t vs $1/T$ for thermolysis and photolysis data gave a single Arrhenius line with $E_i - E_t = 4.6 \pm 0.2$ kcal mol^{-1} and $A_i/A_t = 10^{3.6\pm0.1}$.

Absolute rate constants for the reactions of phenylchlorocarbene with TME in isooctane, acetonitrile, and toluene at room temperature are 2.8×10^8, 1.1×10^8, and 1.4×10^8 M^{-1} s^{-1}, respectively.[3] Additionally, the absolute rate constants for the reactions of phenylchlorocarbene with 1-hexene, diethyl fumarate, and ethyl acrylate in toluene or ethyl acetate are similar,[4] indicating that the cycloadditions are not sensitive to solvent polarity and hence no significant change in the E_t. If E_t is taken[8] to be −1.7 kcal mol^{-1} and $A_t = 1.9 \times 10^7$ M^{-1} s^{-1}, the kinetic parameters for 1,2-H shift for benzylchlorocarbene in CH$_3$CN can be calculated, hence, k_i(CH$_3$CN) = $10^{11.0}$ exp −(2900 cal/mol/RT)s^{-1}. In an earlier paper,[2] we reported k_i(isooctane) = $10^{12.2}$ exp −(6400 cal/mol/RT)s^{-1}, which predicts a life-time for $C_6H_5CH_2\ddot{C}Cl$ in the order of 40 ns at room temperature, which is in excellent agreement with LFP[9] data of 30 ns. Recently, it was shown[1] that 1,2-H shift in Bz$\ddot{C}$Cl involves a charge development in the transition state. In the present study, the lowering of activation energy by ~3 kcal mol^{-1} for 1,2-H shift of Bz$\ddot{C}$Cl in CH$_3$CN as compared to isooctane can be explained in terms of the increased stability of such a charge-developed transition state by CH$_3$CN. While our finding is in broad agreement with the work of Tomioka et al.[10] the marked

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Table I. Product Distribution in the Photolysis and Thermolysis of 1 in TME (CH_3CN Solvent)

	hν 20.8 °C		*hν* 25.1 °C		*hν* 29.9 °C		*hν* 35.8 °C		*hν* 44.1 °C		*hν* 49.2 °C		Δ 82.0 °C		Δ 91.5 °C	
[TME], M	*Z*/*E*	3/2	*Z*/*E*	3/2	*Z*/*E*	3/2	*Z*/*E*	3/2	*Z*/*E*	3/2	*Z*/*E*	3/2	*Z*/*E*	3/2	*Z*/*E*	3/2
0.1	0.41	0.0632	0.43	0.0619	0.43	0.0476	0.41	0.0435	0.43	0.0367	0.43	0.0333	0.22	0.0163		
0.2	0.40	0.129	0.42	0.125	0.40	0.0959	0.40	0.0864	0.42	0.0714	0.42	0.0660	0.22	0.0360	0.40	0.0306
0.8	0.42	0.454	0.42	0.431	0.43	0.375	0.41	0.316	0.42	0.273	0.41	0.252	0.22	0.154	0.43	0.126
1.1	0.44	0.585	0.43	0.560	0.42	0.480	0.41	0.426	0.42	0.369	0.41	0.333	0.21	0.205	0.42	0.169
1.4	0.45	0.797	0.46	0.756	0.42	0.551	0.41	0.479	0.43	0.469	0.41	0.401	0.21	0.304	0.42	0.254
2.0	0.47	0.954	0.47	0.932	0.43	0.675	0.41	0.553	0.43	0.512	0.41	0.475	0.19	0.417	0.43	0.340
2.6	0.49	1.183	0.49	1.172	0.44	0.735	0.43	0.694	0.43	0.605	0.42	0.579	0.17	0.607	0.44	0.475
3.2	0.50	1.387	0.50	1.342	0.44	0.867	0.43	0.730	0.43	0.667	0.43	0.662	0.16	0.758	0.44	0.596
$\frac{k_i}{k_t}$ =	1.65 ± 0.010		1.68 ± 0.006		2.17 ± 0.025		2.36 ± 0.022		2.83 ± 0.031		3.17 ± 0.025		6.65 ± 0.123		6.99 ± 0.025	

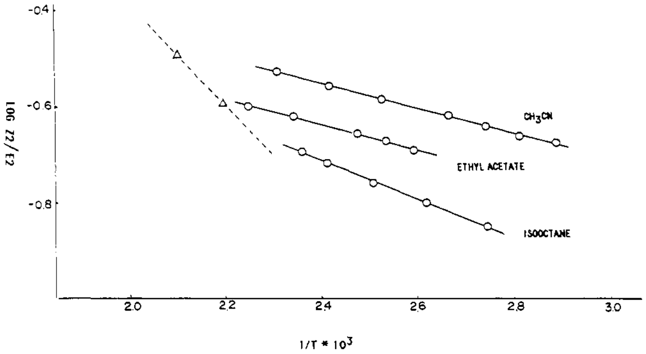


Figure 1. Log Z2/E2 vs 1/*T* plot: (△) equilibrium data from ref 11; (○) present data.

difference in the relative reactivities of BzC̈Cl toward TME (k_i/k_t = 1.68 in CH_3CN and k_i/k_t = 0.1 in isooctane at 25 °C) and the invariance in the absolute rate constants for carbene–alkene cycloadditions with increasing solvent polarity do not conform with the carbene–acetonitrile intermediacy. Also, the migration of the benzylic C–H σ-bond to the carbenic carbon in benzylchlorocarbene–acetonitrile intermediate (ylide) would be energetically a less favored process due to the development of a negative charge on the carbenic carbon. Moreover, for such a process the k_i/k_t in CH_3CN should be expected to be much less than what has been observed. While the recent kinetic data[10] suggested a carbene–acetonitrile intermediate, there is no evidence from the present studies that leads us to infer its existence. Increase in *Z*/*E* ratio with increase in cyclopropanation is reported.[1] Since cyclopropanation does not compete well with 1,2-H migration in CH_3CN, the increase in *Z*/*E* ratios as a function of [TME] should be expected to be minimal. This has actually been observed and the increase in *Z*/*E* ratios with increasing concentration of TME is only marginal.

Prochazka et al.[11] studied the thermal equilibrium of (*Z*)- and (*E*)-β-chlorostyrenes by heating (180–200 °C) a 9:1 mixture of the *Z* and *E* isomers (iodine catalyzed) for about 10 h. The iodine was removed and the β-chlorostyrenes analyzed. The *Z*/*E* ratios for these experiments are plotted in Figure 1. Least-squares analysis of log *Z*/*E* vs 1/*T* gave a value of 4.5 kcal mol^{-1} for Δ*H*, which indicates that the *E* isomer is stabilized by this amount in comparison with the Z isomer.[11]

Z/*E* ratios of β-chlorostyrenes 2 obtained from thermal decomposition of 1 in various solvents are given in Table II and Figure 1.

Firstly, the ratios of Z2/E2 derived from the decomposition of 1 are markedly different from the data obtained by thermal equilibrium method and hence are not thermodynamically controlled. The *Z*/*E* ratios show a marginal temperature dependence and this dependence is slightly greater in nonpolar solvent. The Z2/E2 ratio increased when the polarity of solvent was increased.

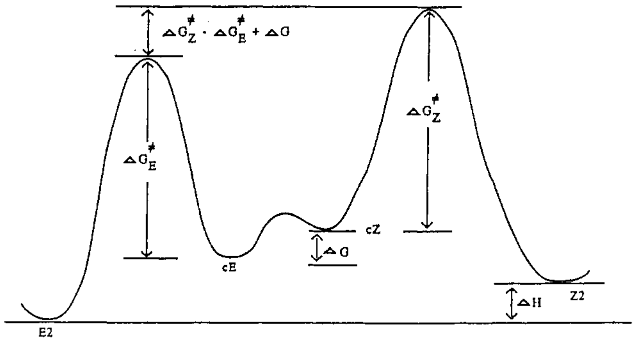
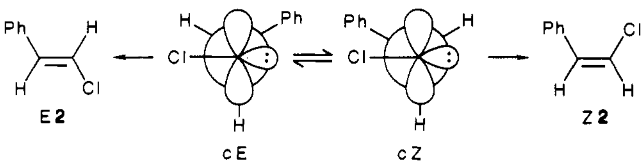


Figure 2. Energy diagram for carbene conformers.

Table II. Temperature Dependence of *Z*/*E* Ratio in the Thermolysis of 3-Benzyl-3-chlorodiazirine

temp, °C	Z2/E2 in isooctane	temp, °C	Z2/E2 in EtOAc	temp, °C	Z2/E2 in CH_3CN
91.0	0.141	112.0	0.204	72.0	0.215
108.2	0.158	121.0	0.214	82.0	0.218
125.2	0.174	131.0	0.222	91.0	0.229
141.6	0.191	153.0	0.241	101.5	0.241
150.6	0.202	170.0	0.251	122.0	0.258
				140.0	0.280
				159.5	0.297

Scheme II



1,2-Hydrogen migration occurs through two limiting conformers cE and cZ. E2 arises from cE and Z2 from cZ (Scheme II). The structure of 3-(1-naphthylmethyl)-3-chlorodiazirine is reported[12] to have the naphthyl group trans to the chlorine atom. It is reasonable to assume a higher preponderance of the trans isomer in 1 and hence an increased population of cE over cZ.

In a kinetically controlled process, the ratio of the product is given by

$$\frac{Z2}{E2} = \frac{k_Z\,[cZ]}{k_E\,[cE]}$$

since k_Z is controlled by $\Delta G^{\ddagger}{}_Z$ and k_E by $\Delta G^{\ddagger}{}_E$, it can be shown that

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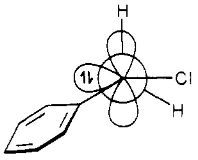
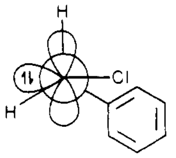
$$\frac{Z2}{E2} = \exp -(\Delta G^{\ddagger}{}_{Z} - \Delta G^{\ddagger}{}_{E} + \Delta G)/RT$$

where $\Delta G^{\ddagger}{}_{Z}$ and $\Delta G^{\ddagger}{}_{E}$ are standard free energies of activation for the formation of Z2 and E2 from cZ and cE, respectively. ΔG is the standard free-energy difference between the two conformers.

Plots of log Z2/E2 vs $1/T$ are displayed in Figure 1. The difference in standard free energies, $\Delta G^{\ddagger}{}_{Z} - \Delta G^{\ddagger}{}_{E} + \Delta G$ is 1.83 ± 0.03 kcal mol^{-1} for isooctane, 1.21 ± 0.06 kcal mol^{-1} for EtOAC, and 1.16 ± 0.04 kcal mol^{-1} for CH_3CN.



cE



cZ

In the cE carbene conformer, the plane of the phenyl ring is coplanar with the C_1–C_2–Cl bond axis. This orientation facilitates the resonance interaction between the phenyl ring and the migrating C–H bond.[13] In the case of the cZ conformer, the plane of the phenyl ring is perpendicular to the C_1–C_2–Cl bond. As a result, resonance interaction is not possible in the latter, hence $\Delta G^{\ddagger}{}_{Z} > \Delta G^{\ddagger}{}_{E}$. If $\Delta G^{\ddagger}{}_{Z}$ is taken[2] to be approximately 2 kcal mol^{-1} higher than $\Delta G^{\ddagger}{}_{E}$ (e.g., $\Delta G^{\ddagger}{}_{Z}$ = 9.5 kcal mol^{-1} and $\Delta G^{\ddagger}{}_{E}$ = 7.5 kcal mol^{-1}), it follows that $\Delta G \sim$ zero from the following relationship, $\Delta G^{\ddagger}{}_{Z} - \Delta G^{\ddagger}{}_{E} + \Delta G = 1.83$ kcal mol^{-1} in isooctane solvent. The barriers to conformer interconversion will be low and the equilibration is rapid. The product ratio Z2/E2 is exclusively determined by the difference in Gibbs function of the two transition states and hence conforms to the Curtin–Hammett principle.[14] The energy diagram (Figure 2) summarizes these relationships.

Experimental Section

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. Peak areas were integrated with a Hewlett-Packard 3390A recorder.

Irradiation was carried out with 3500-W UV lamps in a Rayonet photoreactor until all the diazirine 1 (0.03 M in solution) was destroyed. Temperature control was within ±0.1 °C. The thermal decomposition of 1 in various concentrations of TME was carried out to 10 half-lives and product ratios were determined at different temperatures. 3-Chloro-3-benzyldiazirine was prepared by Graham's method[7] and purified by chromatography on silica gel. Absence of chlorostyrene prior to photolysis or thermolysis was confirmed by ^{1}H NMR spectroscopy.

Product Studies. 3-Chloro-3-benzyldiazirine (2.5×10^{-3} mol) and TME (0.116 mol) were dissolved in dry acetonitrile (100 mL) and the solution was photolyzed for 4 h at 15 °C. The unreacted TME and solvent were distilled off under reduced pressure. The chlorostyrene and cyclopropane were analyzed by GC. The residue was chromatographed on a column of silica gel (25 mm × 300 mm) and eluted with hexane and 2% hexane–ethyl acetate. In every instance, the chlorostyrene 2 were eluted in the first 200 mL of the solvent and the fractions contained the cyclopropane 3. The ^{1}H NMR of both styrene and the cyclopropane compared well with the reported data.[1] The yield of cyclopropane was 23.5% on the basis of the amount of diazirine used. Authentic samples of 3 and 2 were used to calibrate GC.

The thermal decompositions of 0.02 M solutions of 1 in acetonitrile, ethyl acetate, and isooctane were carried out to 10 half-lives and the product ratios were determined at different temperatures.

Acknowledgment. M. T. H. Liu thanks NSERC of Canada and U.P.E.I. for financial support and K. Charlesworth for preliminary experiments.

Note added in proof: Our recent work on LFP of 3-chloro-3-(*p*-nitrophenyl)diazirine indicated that (nitrophenyl)chlorocarbene reacts with pure CH_3CN to form nitrile ylide with $k_{\text{ylide}} \simeq 10^5$ M^{-1} s^{-1}. It is possible that BzCCl can also form ylide with CH_3CN in the absence of other substrates. The values for k_i and k_t are at least 2–3 orders of magnitude larger than k_{ylide}; therefore the formation of nitrile ylide in the BzCCl system is not significant as suggested in the text.

Registry No. 1, 88211-05-6; TME, 563-79-1; benzylchlorocarbene, 88211-07-8.

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Synthesis of 8-(Methoxycarbonyl)[6]paracyclophane-3,4-dione

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The chemistry of small-bridged [*n*]paracyclophanes has attracted much attention in recent years[1] as exemplified by the spectroscopic characterization of [5]paracyclophane[2] and even lower [4] congener.[3] The smallest bridged cyclophane that has been isolated thus far is [6]paracyclophane (**1a**) and its derivatives.[4] Although many derivatives of larger bridged [7]–[8]paracyclophanes having functional groups on the bridge have been synthesized,[1,5] little is known of the [6] derivatives. Tochtermann has reported the synthesis and conformation of the 3-hydroxy and 3-keto derivatives.[6] We have succeeded in synthesizing (*Z*)-[6]paracycloph-3-ene (**2**) and its derivatives having a cis double bond in the bridge and found remarkable effect of the double bond on the physical and chemical properties of this system.[7] As an extension of

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