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Rearrangement of Alkylchlorocarbenes: 1,2-H Shift in Free Carbene, Carbene−Olefin Complex, and Excited States of Carbene Precursors

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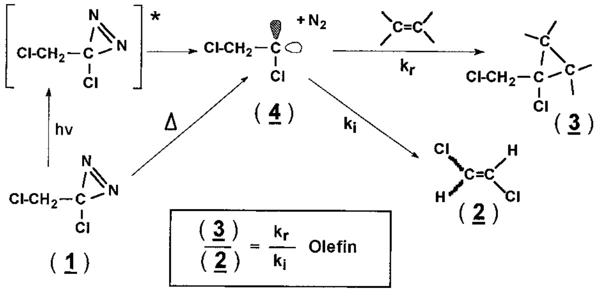
Abstract: Photolysis of alkylchlorodiazirines (**1**) in the presence of olefins gives a cyclopropane (**3**) by addition of the generated carbene to the olefin and a vinyl chloride derivative (**2**) resulting from a 1,2-H shift rearrangement. This rearrangement may occur either in the carbene or in some excited state, precursor of the carbene (RIES mechanism), or in a "carbene + olefin complex" on the way to the formation of **3** (COC mechanism). Results obtained by time-resolved photoacoustic calorimetry as well as by thermolysis and photolysis of $ClCH_2C(N_2)Cl$ and $CH_3(CH_2)_2C(N_2)Cl$ in the presence of tetramethylethylene clearly indicate that both the RIES and COC mechanisms play a role but with efficiencies which greatly depend on the nature of the diazirine. Reexamination of the results previously obtained with benzylchlorodiazirines indicates that, for this class of diazirines, the RIES mechanism is temperature dependent and has a very low efficiency at room temperature and below, whereas the nonlinearity of the plots [**3**]/[**2**] *vs* [olefin] is mainly due to the COC mechanism.

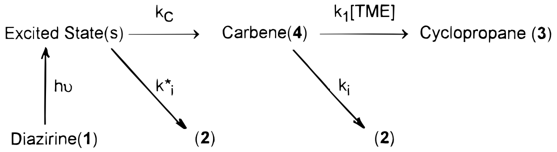
Introduction

Alkylchlorocarbenes with a C−H bond in the α position of the carbene center, **4**, which may be produced by photolysis or thermolysis of diazirines, **1**, generally undergo a fast 1,2-H migration (rate constant k_i) to give a vinyl chloride derivative, **2**. In recent years, much information has been obtained on the kinetics of this process.[1] This rearrangement is in competition with intermolecular reactions such as addition to olefins (rate constant k_r) to give a cyclopropane, **3**. The simplest mechanism to describe the system, given in Scheme 1, predicts a linear relation between the ratio [**3**]/[**2**] and the concentration of the olefinic reactant, [olefin].

Scheme 1



Scheme 2



But the distribution of the products obtained under either photolysis or thermolysis do not fit this simple mechanism. Plots of [**3**]/[**2**] *vs* [olefin] are curved, indicating that, at high concentrations of olefin reactant, the amount of [**2**] is larger than expected (Figure 1). This has been explained by either a rearrangement in excited states (RIES) or by a 1,2-H migration in a diazo intermediate or by the formation of a carbene−olefin complex (COC).

The RIES mechanism is supported by the fact that, in the absence of olefin, the rearrangement products obtained by thermolysis and by photolysis of some diazirines show a quite different distribution of isomers.[2] The more recent observations made by several research groups[3,4] also lend support to the RIES mechanism shown in Scheme 2.

With $\alpha = k_C/(k^*_i + k_C)$ being the yield of formation of the carbene, this mechanism which may be invoked only in the case of photolysis gives

$$[\mathbf{2}]/[\mathbf{3}] = k^*_i/k_C + [k_i/(\alpha k_1)]/[\text{olefin}]$$

The nature of the excited state(s) involved in this process is uncertain. It could be the following: (i) The excited state of diazirines, which may have a nonnegligible lifetime since the fluorescence of several akyldiazirines has been reported.[4] Theoretical studies indicate that several reaction pathways are

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(1) (a) Moss, R. A. *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI: Greenwich, CT, 1994; Vol. 1. (b) Jackson, J. E.; Platz, M. S. *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI: Greenwich, CT, 1994; Vol. 1. (c) Liu, M. T. H. *Acc. Chem. Res.* **1994**, *27*, 287. (d) Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84.

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(4) (a) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034. (b) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 8985.

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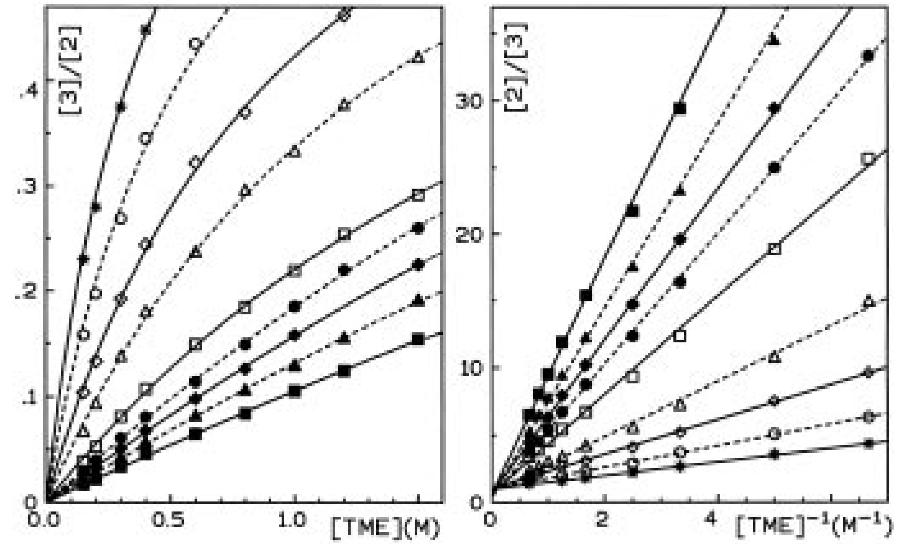


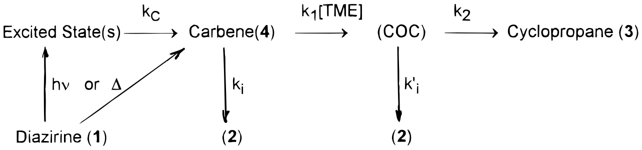
Figure 1. (a) Plots of the ratio [**3**]/[**2**] *vs* [TME] for *n*-propylchlorodiazirine + TME in isooctane, under photolysis at 10 °C (*), 20 °C (○), 30 °C (◇), 40 °C (△) and 55 °C (□) and under thermolysis at 79 °C (●), 84 °C (◆) 90 °C (▲), and 97 °C (■). (b) Plots of the ratio [**2**]/[**3**] *vs* 1/[TME] for the same system, with same conditions and symbols.

possible from the excited state of a diazirine.[5] Although the only paths considered were those leading to (carbene + N_2) and to a diazo compound as products, the complexity of the system of energy surfaces makes quite plausible an H migration, more or less concerted with extrusion of N_2. (ii) An excited state of the carbene may also, from an energetic point of view, be produced from the excited state of the diazirine and has been proposed as a possible intermediate for this kind of rearrangement.[6a] (iii) An excited state of a diazo intermediate, the adiabatic formation of which is thermodynamically feasible.

The photolysis of diazirines gives, with variable efficiencies, diazo compounds. In the case of chlorodiazirines, this efficiency is low and the chlorodiazo derivatives are unstable, even at low temperature. For instance, photolysis of a benzylchlorodiazirine in 3-methylpentane at 100 K[6b] or in argon matrix at 10 K[6c] gives "traces of benzylchlorodiazomethane", observed by IR spectroscopy, but this diazo compound rapidly disappears at 200 K.[6b] Similar results were reported for the photolysis of phenylchlorodiazirine in argon matrix at 10 K.[6d] One of the referees suggested that this decomposition of the diazo produces **2**: this pathway would bypass the carbene in a similar manner as the RIES process, but it could still be operating in thermolysis (if the thermolysis of diazirines produces diazo ground state). However, the global yield of formation of **2** *via* the diazo ground state pathway is probably negligible for alkylchlorodiazirines since (i*)* the reported "traces of benzylchlorodiazomethane" probably represent a yield of formation lower than 5 or 10% and (ii) the thermal decomposition of a diazo (possibly acid catalyzed) would give not only the rearranged product (**2**) but also the carbene (**4**) which could even be the major product.

The COC mechanism, represented in Scheme 3, has been suggested by Skell *et al.*,[7a] Turro *et al.*,[7b] and Tomioka *et al.*[7c]

Scheme 3



Theoretical calculations[8] give a well-defined orientation between dihalocarbenes and olefin, even at long distance, but predict no minimum on the free energy profile connecting the separated species and cyclopropane. However these profiles are strongly dependent on the nature of the carbene: at the distance corresponding to the postulated complex, the ΔG curve present a sharp maximum for CCl_2 but is nearly flat for CBr_2. It seems possible that the same type of calculations would yield a mimimum for alkylchlorocarbenes.

In 1987, M. T. H. Liu[9] used the COC mechanism to explain the curvature of the plots of [**3**]/[**2**] *vs* [olefin] obtained under thermolysis and photolysis of benzylchlorodiazirines in the presence of various olefins. In this mechanism, the COC could be a "π-complex", with bonding interactions between the empty orbital of the carbene and the filled olefinic π-orbital and/or between the filled orbital of the carbene and the empty olefinic π*-orbital. Furthermore, because the temperature dependence of the ratio (k_i/k_1) measured under photolysis and thermolysis gives a single Arrhenius line, Liu concluded that the RIES mechanism was inefficient in the case of benzylchlorocarbenes.

With the olefin being tetramethylethylene (TME) and $\beta = k_2/(k'_i + k_2)$ being the yield of formation of **3** from the COC, this mechanism gives

$$[\mathbf{2}]/[\mathbf{3}] = k'_i/k_2 + [k_i/(\beta k_1)]/[\mathrm{TME}] = (1-\beta)/\beta + [k_i/(\beta k_1)]/[\mathrm{TME}]$$

With both the RIES and COC mechanisms being efficient,

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(7) (a) Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 7131. (b) Turro, N. J.; Lehr, G. F.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* **1982**, *104*, 1754. (c) Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Am. Chem. Soc.* **1984**, *106*, 454.

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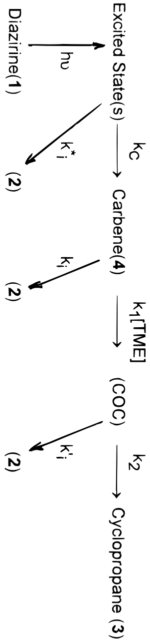
(9) (a) Liu, M. T. H.; Soundararajan, N.; Paike, N.; Subramanian, R. *J. Org. Chem.* **1987**, *52*, 4223. (b) Liu, M. T. H.; Suresh, R. V.; Soundararajan, N.; Vessey, E. G. *J. Chem. Soc., Chem. Commun.* **1989**, 12.

Scheme 4



Scheme 4 yields the relation

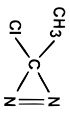
$$[\mathbf{2}]/[\mathbf{3}] = (1 - \beta)/\beta + k^*_i/(\beta k_C) + [k_i/(\alpha\beta k_1)]/[\mathrm{TME}]$$

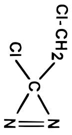
Thus, in all cases, the plot of [**2**]/[**3**] *vs* 1/[TME] must be linear but (i) the slopes of the plots obtained under thermolysis ($k_i/(\beta k_1)$) and photolysis ($k_i/(\alpha\beta k_1)$) must differ by a factor α and (ii) the intercepts, ([**2**]/[**3**])$_\infty$ (value of [**2**]/[**3**] when [TME] → ∞), must be larger under photolysis than under thermolysis, by an amount equal to ($k^*_i/(\beta k_C)$) = (1 − α)/αβ.

This paper presents the results obtained by time-resolved photoacoustic calorimetry as well as by thermolysis and photolysis of $ClCH_2C(N_2)Cl$ and $CH_3(CH_2)_2C(N_2)Cl$ in the presence of TME. These results clearly indicate that both the RIES and COC mechanisms play a role, but with efficiencies which depend on the nature of the considered diazirine. Reexamination of the results previously obtained with benzylchlorodiazirines confirms that, for this class of diazirines, the nonlinearity of the plots [**3**]/[**2**] *vs* [TME] is mainly due to the COC mechanism. But it also reveals that a RIES mechanism, temperature-dependent and poorly efficient (especially at room temperature and below), cannot be neglected.

Experimental Section

Diazirines $XCH_2C(N_2)Cl$ with X = H (**1a**), Cl (**1b**), CH_3CH_2 (**1c**), C_6H_5 (**1d**), *p*-ClC_6H_4 (**1e**), and *p*-MeC_6H_4 (**1f**) were prepared by the hypochlorite oxidation of the corresponding amidines.[10] Tetramethylethylene was purchased from Aldrich and used without purification. Irradiation was carried out with 350 nm UV lamps in a Rayonet photoreactor until all the diazirine was destroyed. The photoacoustic apparatus has been previously described.[11]


1a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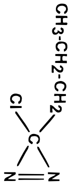
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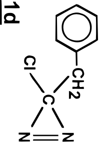
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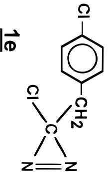
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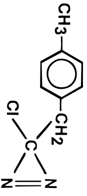
1f

Details on the analysis and identification of the products and on the photoacoustic measurements are given as Supporting Information.

Results

Photolysis and Thermolysis. The relative amounts of products obtained under photolysis and thermolysis of diazirines **1b** and **1c** in the presence of various concentrations of TME at several temperature are given in Tables 1 and 2 as ratios of [**3**]/[**2**] and [**2-E**]/[**2-Z**]. Previously published data[9] were used for comparing diazirines **1d**−**f** with diazirines **1b** and **1c**.

Photoacoustic. Photoacoustic calorimetry (PAC) monitors the amplitude and time evolution of heat depositions in a system following photoexcitation. This information can provide kinetic

Table 1. Ratios [**3**]/[**2**] and (*E*/*Z*) Obtained for the Photolysis and Thermolysis of $ClCH_2C(N_2)Cl$ in the Presence of TME

[TME] (M)	0 °C		10 °C		18 °C		30 °C		45 °C		52 °C		75 °C		95 °C		102 °C		110 °C	
	[**3**]/[**2**]	(*E*/*Z*)	[**3**]/[**2**]	(*E*/*Z*)	[**3**]/[**2**]	(*E*/*Z*)	[**3**]/[**2**]	(*E*/*Z*)	[**3**]/[**2**]	(*E*/*Z*)	[**3**]/[**2**]	(*E*/*Z*)	[**3**]/[**2**]	(*E*/*Z*)	[**3**]/[**2**]	(*E*/*Z*)	[**3**]/[**2**]	(*E*/*Z*)	[**3**]/[**2**]	(*E*/*Z*)
0.00		(0.190)		(0.184)		(0.182)		(0.176)		(0.180)		(0.175)		(0.065)		(0.064)		(0.062)		(0.065)
0.03	0.639	(0.282)	0.510	(0.271)	0.436	(0.270)	0.322	(0.241)	0.222	(0.228)	0.215	(0.233)	0.330	(0.086)	0.164	(0.074)	0.143	(0.071)	0.125	(0.071)
0.06	0.757	(0.307)	0.680	(0.292)	0.638	(0.287)	0.513	(0.269)	0.361	(0.240)	0.347	(0.255)	0.625	(0.110)	0.320	(0.086)	0.275	(0.082)	0.250	(0.081)
0.10	0.814	(0.306)	0.760	(0.294)	0.745	(0.301)	0.611	(0.285)	0.515	(0.268)	0.457	(0.258)	1.00	(0.140)	0.510	(0.102)	0.450	(0.096)	0.390	(0.093)
0.15	0.849	(0.310)	0.791	(0.315)	0.785	(0.308)	0.675	(0.294)	0.587	(0.288)	0.545	(0.276)	1.41	(0.170)	0.770	(0.122)	0.670	(0.112)	0.590	(0.106)
0.20	0.869	(0.312)	0.820	(0.310)	0.793	(0.310)	0.721	(0.296)	0.645	(0.291)	0.597	(0.282)	1.78	(0.206)	1.00	(0.140)	0.880	(0.127)	0.780	(0.120)
0.30			0.836	(0.308)	0.803	(0.308)	0.745	(0.294)	0.676	(0.297)	0.642	(0.289)	2.49	(0.267)	1.42	(0.176)	1.27	(0.156)	1.13	(0.145)
0.40	[0.865	(0.305)]	0.843	(0.307)	0.816	(0.304)			0.690	(0.292)	0.672	(0.287)	3.00	(0.316)	1.74	(0.204)	1.60	(0.183)	1.44	(0.168)
0.60	[0.852	(0.295)]	[0.818	(0.296)]	[0.805	(0.298)]	[0.743	(0.292)]	0.699	(0.294)	0.739	(0.291)	3.63	(0.380)	2.20	(0.245)	2.07	(0.227)	1.88	(0.206)
0.80	[0.800	(0.285)]	[0.820	(0.297)]	[0.802	(0.285)]	[0.766	(0.280)]	[0.694	(0.285)]	0.764	(0.279)	3.93	(0.412)	2.50	(0.270)	2.39	(0.257)	2.19	(0.235)
slope[b]	0.01455		0.0235		0.0296		0.0525		0.0809		0.1004		0.0797		0.1585		0.1780		0.2147	
intercept[b]	1.080		1.110		1.116		1.138		1.128		1.197		0.148		0.195		0.178		0.181	

[a] Values given here were obtained, in fact, by nonlinear regression of the curves [**3**]/[**2**] *vs* [TME], the values in brackets not taken into account for the calculations. [b] Slopes and intercepts of the linear plots of [**2**]/[**3**] *vs* 1/[TME]. With the full set of data (including the bracketed values) the intercept values would not be significantly different but slightly larger (1.137, 1.128, 1.119, 1.150, 1.129, and 1.197).

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

(11) (a) LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877. (b) LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 712.

Table 2. Ratios [**3**]/[**2**] and (E/Z) Obtained for the Photolysis and Thermolysis of $CH_3(CH_2)_2C(N_2)Cl$ in the Presence of TME

[TME] (M)	0 °C		10 °C		20 °C		30 °C		40 °C		55 °C		79 °C		84 °C		90 °C		97 °C	
	[3]/[2]	(E/Z)	[3]/[2]	(E/Z)	[3]/[2]	(E/Z)	[3]/[2]	(E/Z)	[3]/[2]	(E/Z)	[3]/[2]	(E/Z)	[3]/[2]	(E/Z)	[3]/[2]	(E/Z)	[3]/[2]	(E/Z)	[3]/[2]	(E/Z)
0.00		(0.477)		(0.490)		(0.492)		(0.497)		(0.502)		(0.503)		(0.413)		(0.412)		(0.424)		(0.419)
0.15	0.301	(0.479)	0.230	(0.485)	0.158	(0.486)	0.104	(0.488)	0.067	(0.491)	0.039	(0.494)	0.030	(0.454)	0.026	(0.442)	0.021	(0.447)	0.017	(0.459)
0.20	0.404	(0.485)	0.280	(0.484)	0.197	(0.489)	0.133	(0.485)	0.093	(0.484)	0.053	(0.488)	0.040	(0.457)	0.034	(0.445)	0.029	(0.453)	0.022	(0.456)
0.30	0.529	(0.494)	0.375	(0.491)	0.269	(0.495)	0.192	(0.484)	0.138	(0.484)	0.081	(0.489)	0.061	(0.483)	0.051	(0.467)	0.043	(0.469)	0.034	(0.479)
0.40	0.62	(0.499)	0.448	(0.496)	0.345	(0.485)	0.244	(0.486)	0.180	(0.478)	0.107	(0.479)	0.081	(0.503)	0.068	(0.485)	0.057	(0.492)	0.046	(0.480)
0.60	0.742	(0.501)	0.55	(0.495)	0.435	(0.486)	0.322	(0.480)	0.237	(0.477)	0.149	(0.478)	0.114	(0.541)	0.098	(0.516)	0.082	(0.510)	0.065	(0.502)
0.80	0.803	(0.490)	0.620	(0.483)	0.506	(0.480)	0.370	(0.480)	0.296	(0.458)	0.184	(0.471)	0.149	(0.587)	0.126	(0.548)	0.106	(0.533)	0.084	(0.528)
1.00	0.845	(0.488)							0.333	(0.464)	0.219	(0.458)	0.185	(0.611)	0.158	(0.578)	0.129	(0.558)	0.105	(0.545)
1.20							0.462	(0.458)	0.377	(0.454)	0.254	(0.443)	0.220	(0.645)			0.155	(0.585)	0.124	(0.563)
1.50			0.717	(0.474)	0.60	(0.482)	0.510	(0.462)	0.422	(0.434)	0.292	(0.449)	0.260	(0.686)	0.225	(0.623)	0.191	(0.600)	0.154	(0.591)
slope[a]	0.321		0.478		0.729		1.213		1.839		3.374		4.802		5.750		6.996		8.859	
intercept[a]	0.85		1.05		1.14		1.15		1.13		1.16		0.617		0.614		0.608		0.628	

[a] Slopes and intercepts of the linear plots of [**2**]/[**3**] *vs* 1/[TME]. Values given here were obtained, in fact, by nonlinear regression of the curves [**3**]/[**2**] *vs* [TME].

Table 3. Experimental Enthalpies and Rate Constants Determined by PAC

diazirine	$\Delta H_1{}^a$	$\Delta H_2{}^a$	$\Delta H_T{}^{a,b}$	k ($\times 10^7$ s^{-1})
1a	−26.1	−39.9	−66.0	0.14
1b	−39.9	−28.8	−68.7	2.0
1d	+3.4	−55.1	−55.1	9.1

[a] Values are in kcal/mol. [b] Total enthalpy of reaction, $\Delta H_T = \Delta H_1 + \Delta H_2$.

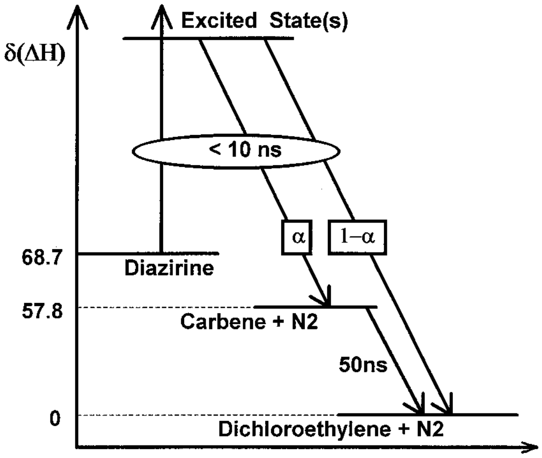

Figure 2. Energetic diagram explaining the principle of the measurements of the RIES efficiency by time resolved-photocacoustic calorimetry.

and enthalpic information about transient intermediates.[11−14] The details of this method have been previously reported.[11,12]

Photoexcitation of diazirine (**1**) initially yields the excited state (**1***), which either directly or via another intermediate rapidly forms (<10 ns) the singlet carbene (**4**) by loss of nitrogen and vinyl halide (**2**) via the RIES process (with 1,2 hydrogen rearrangement and loss of nitrogen). Experimentally, photoexcitation of **1a**, **1b**, and **1d** in heptane results in two heat depositions: the first one, ΔH_1, is fast ($\tau < 5$ ns) and reflects carbene and vinyl halide formation from the diazirine; the second, ΔH_2, is slower ($\tau = 1/k$) and is due to vinyl halide formation by rearrangement of the carbene. The PAC reaction enthalpies can be determined from $\Delta H_1 = (1 - a_1)\, E_{h\nu}$ and $\Delta H_2 = -a_2 E_{h\nu}$, where $E_{h\nu}$ is the incident photon energy, 84.8 kcal/mol, and a_n is the fraction of incident photon energy lost to the solution in the given heat deposition.

Deconvolution of the PAC waveforms yields the values of ΔH_1, ΔH_2, and k which are given in Table 3. The rate constants for the 1,2-H rearrangement of **4a** and **4d** obtained by PAC are similar to those determined by nanosecond absorption spectroscopy.

Assuming that the overall quantum efficiency for the formation of **2** is unity, then **1*** can form the carbene **4** and the vinyl halide **2** with efficiencies α and (1 − α) respectively (Figure 2). The value of α can be determined using the equation $\alpha = \Delta H_2/\Delta H_r$ (**4** → **2**), which is simply the ratio of the obtained

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(12) (a) Rudzki, J. E.; Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 7849. (b) Westrick, J. A.; Goodman, J. L.; Peters, K. S. *Biochemistry* **1987**, *22*, 8313.

(13) (a) Heihoff, K.; Braslavsky, S. E.; Schaffner, K. *Biochemistry* **1987**, *22*, 1422. (b) Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1987**, *109*, 5267. (c) Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090. (d) Ni, T.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 457.

(14) PAC measures the total volume change of the associated reaction. This includes thermal, ΔV_{th}, and reaction, ΔV_{rx}, volume changes. In the reaction (**1** → **4**), ΔV_{rx} should be posititive which would give an erroneously large value for ΔH_1. However, ΔV_{rx} should be small for the reaction (**4** → **2**) so that ΔH_2 should accurately reflects the thermal volume change.

Table 4. Calculated ΔH_r (**4** → **2**) and Efficiency of Carbene Formation

diazirine	ΔH_f (**4**)[a,b]	ΔH_f (**2**)[b]	ΔH_r (**4** → **2**)[b]	α
1a	61.2	8.6[c]	−52.6	0.76
1b	59.6	1.1[c]	−58.5	0.49
1d	87.2	28.4[a]	−58.8	0.94

[a] PM3 values obtained using Spartan, ver. 3.1, Wavefunction, Inc., 1994. [b] Values are in kcal/mol. [c] See: Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

PAC enthalpy to that of the known heat of reaction. Unfortunately, ΔH_r (**4** → **2**) has not been determined for these carbenes but can be calculated by using the values of ΔH_f (**2**) and ΔH_f (**4**) given in Table 4. When not available from the literature, the values of ΔH_f were calculated using the PM3 method which usually gives results in agreement with experimental values within a few kcal/mol. The value of α for **1a**, 0.67, is similar to that obtained previously[3a] using TME as trapping agent for the carbene and suggest that the value used for ΔH_r (**4** → **2**) is reasonable.

Interpretation and Discussion

Determination of the RIES Efficiency. The PAC method gives α = 0.49, 0.76, and 0.94 for $ClCH_2C(N_2)Cl$, $CH_3C(N_2)Cl$, and $C_6H_5CH_2C(N_2)Cl$, respectively (see Table 4), indicating that the efficiency of the RIES process, $\Phi_{RIES} = (1 - \alpha)$, greatly depends on the structure of the diazirine. The exact value of α depends on the value of ΔH_r (**4** → **2**) which can be calculated from the values of ΔH_f (**2**) and ΔH_f (**3**), obtained by theoretical chemistry methods.

The value $\Phi_{RIES} = 0.24$ thus obtained for **1a** is similar to the 0.33 yield of vinyl chloride found[3a] under photolysis of **1a** + TME when [TME] → ∞. The difference may be due to some vinyl chloride produced, in the later case, via the COC mechanism, but this clearly indicates the limits of the PAC method when the value of ΔH_r is not experimentally well determined by some reliable experimental method. It is therefore of interest to compare the values of α deduced from PAC measurements with those which may be obtained from product analysis.

It has been shown above that the slopes of the plots of [**2**]/[**3**] *vs* 1/[TME] obtained under photolysis ($k_i/(\alpha\beta k_1)$) and thermolysis ($k_i/(\beta k_1)$) must differ by a factor α and that the intercepts of these plots, ([**2**]/[**3**])$_\infty$, must be larger under photolysis than under thermolysis, by an amount equal to $(k^*_i/(\beta k_C)) = (1 - \alpha)/(\alpha\beta)$. This provides two methods to estimate the value of α, but since photolysis and thermolysis are usually not performed to the same temperature, measurements must be made at various temperatures for both methods and the results should then be extrapolated to a common temperature.

The value of ([**2**]/[**3**])$_\infty$ obtained by photolysis and thermolysis of diazirines **1b**, **1c**, and **1f** in the presence of TME are plotted *vs* the temperature in Figure 3. There is no measurable difference between the values under photolysis and thermolysis in the case of **1f**, but differences around 0.96 and 0.50 are obtained for **1b** and **1c**, respectively. With the values of the intercept under thermolysis, ([**2**]/[**3**])$_\infty$ = $(1 - \beta)/\beta$, this method gives

$$\beta \approx 0.85 \quad \text{and} \quad \alpha \approx 0.54 \quad \text{for} \quad ClCH_2C(N_2)Cl$$

$$\beta \approx 0.62 \quad \text{and} \quad \alpha = 0.72 \quad \text{for} \quad CH_3(CH_2)_2C(N_2)Cl$$

$$\beta \approx 0.77 \quad \text{and} \quad \alpha \approx 1.00 \quad \text{for} \quad ClC_6H_4CH_2C(N_2)Cl$$

Similar values can be obtained for α by considering the difference between the slopes of the plots [**2**]/[**3**] *vs* 1/[TME] measured under photolysis ($k_i/(\alpha\beta k_1)$) and thermolysis ($k_i/(\beta k_1)$). But since the processes related to k_i and k_1 have quite different activation energies, these slopes are strongly temperature dependent. The shift between the corresponding Arrhenius lines must be equal to log α. This is shown in Figure 4 where the log of the slope of the plots [**2**]/[**3**] *vs* 1/[TME] is plotted *vs* 1/*T*, for **1b**, **1c**, and **1e**.

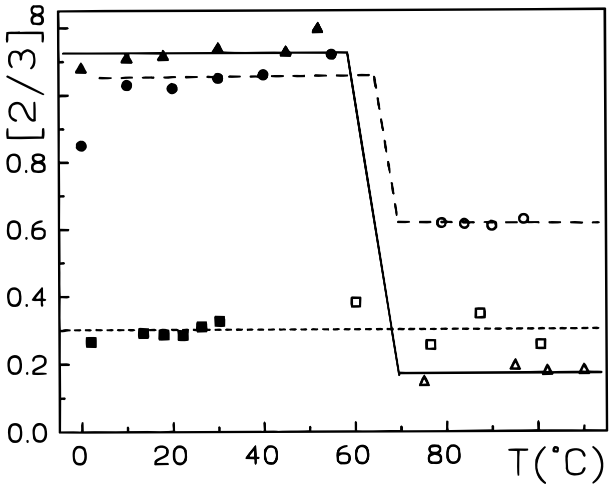


Figure 3. Values of ([**2**]/[**3**])$_\infty$ *vs* temperature for the diazirines **1b** (△ and ▲), **1c** (○ and ●), and **1f** (□ and ■) under thermolysis (open symbols) and photolysis (closed symbols). These values of the ratio [**2**]/[**3**] when [TME] → ∞ are obtained from the intercepts of plots such as shown in Figure 1b.

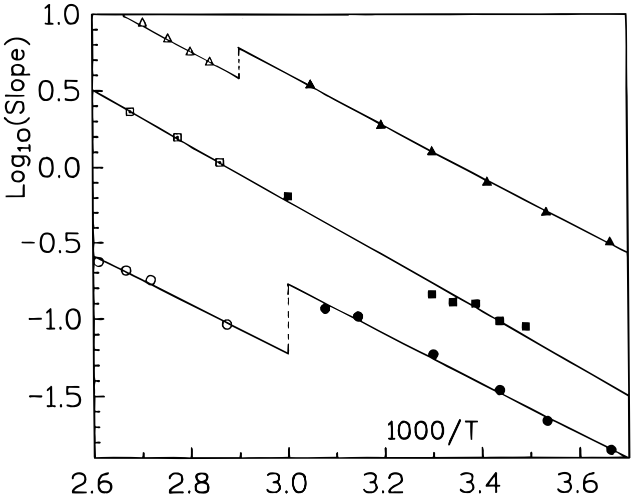


Figure 4. Arrhenius plots for the diazirines **1b** (△ and ▲), **1c** (○ and ●) and **1e** (□ and ■, upshifted by 0.3 unit) under thermolysis (open symbols) and photolysis (closed symbols). The "slope" used on the *Y*-axis is the slope of the plots of [**2**]/[**3**] *vs* 1/[TME], equal to ($k_i/(\beta k_1)$) under thermolysis and to ($k_i/(\alpha\beta k_1)$) under photolysis (see equations related to Scheme 4).

For $ClCH_2C(N_2)Cl$ and $CH_3(CH_2)_2C(N_2)Cl$, the Arrhenius line obtained under photolysis is shifted with respect to the line obtained under thermolysis ; the amplitude of this shift gives α ≈ 0.42 and 0.62, respectively. On the contrary, the efficiency of the RIES process must be very small for $ClC_6H_4CH_2C(N_2)Cl$ (and other benzylchlorodiazirines) because data obtained under photolysis and thermolysis fall on the same line as previously noticed.[9a]

On the Existence and the Properties of a COC. The RIES process can explain, at least in part, the non linear plots of [**3**]/[**2**] *vs* [olefin] obtained under photolysis of some diazirines in the presence of olefins, but this process cannot be invoked for data obtained by thermolysis. In fact, under thermolysis, the amount of **2** produced from the COC and responsible for the curvature is usually very small, compared to the total amount of **2**, because the 1,2 rearrangement of the free carbene is very fast at high temperature. Consequently, in many cases, the curvature of the plots of [**3**]/[**2**] *vs* [olefin] is rather faint and the accuracy of the value of $([\mathbf{2}]/[\mathbf{3}])_\infty$ is rather poor. But the thermolysis of the system $CH_3(CH_2)_2C(N_2)Cl$ + TME gives plots of [**3**]/[**2**] *vs* [TME] which are clearly curved (see Figure 1) and the intercept of the plots [**2**]/[**3**] *vs* 1/[TME], ~0.618 ± 0.010, differs from zero by an amount which is far beyond all possible experimental incertitudes.

For benzylchlorocarbenes, it seems well established that the efficiency of the RIES process is either zero or, with a reasonable limit for the incertitude on experimental measurements, less than 10−15%.

Under photolysis of benzylchlorodiazirines in the presence of some olefins, the curvature of the plots of [**3**]/[**2**] *vs* [olefin] is very clear, far beyond possible experimental errors, yielding for instance values of $([\mathbf{2}]/[\mathbf{3}])_\infty$ which are around 0.3, 0.6, 2.0, and 3.0 for the photolysis at 24 °C of **1d** with TME, α-chloroacrylonitrile (Cl-ACN), diethyl fumarate (DEF), and diethyl mesaconate (MES), respectively.[15] Such large values of $([\mathbf{2}]/[\mathbf{3}])_\infty$ corresponding to 23, 37, 66, and 75% of **2** cannot be explained by a RIES process with an efficiency < 10−15%. Furthermore, the RIES process should give the same amount of **2** whatever the olefin is so that $([\mathbf{2}]/[\mathbf{3}])_\infty$ should be independent of the nature of the olefin unless the RIES efficiency is dependent on the solvent polarity. This does not seem to be the case since there is no apparent correlation between the values of $([\mathbf{2}]/[\mathbf{3}])_\infty$ and the polariries of TME, Cl-ACN, DEF, and MES.

Another demonstration of the existence of a COC (as well as another confirmation of the efficiency of the RIES process) may be obtained from the changes in the distribution of the *E* (*trans*) and *Z* (*cis*) isomers of the rearrangement product, **2-E** and **2-Z**, as a function of the concentration of the olefin reactant. These changes are indeed quite large for the system TME + $ClCH_2C(N_2)Cl$.

In the absence of olefin reactant, the thermolysis of $ClCH_2C(N_2)Cl$ gives a mixture of (*Z*)- and (*E*)-dichloroethylene with an *E*/*Z* ratio ≈ 0.065, (nearly) independent of the temperature on the range (75−110 °C). Therefore the rearrangement of the free carbene $ClCH_2CCl$ gives ~6% of **2-E** and ~94% of **2-Z**.

Photolysis of the same diazirine in the absence of olefin reactant also gives dichloroethylene with an *E*/*Z* ratio (nearly) independent of the temperature on the range (0−52 °C), but this ratio is now equal to 0.18, i.e. ~15% of **2-E** and ~85% of **2-Z**. This is explained by the RIES process which produces **2** with a much larger *E*/*Z* ratio than the free carbene. If the efficiency of RIES is ~52%, then the RIES process gives ~25% of **2-E** and ~75% of **2-Z**.

Upon addition of TME, both the ratios **2-E**/**2-Z** and **3**/**2** increase, and as shown in Figure 5, there is a clear correlation between these changes, independent of the temperature but strongly dependent on the method, photolysis or thermolysis, used to drive the reaction.

A common intermediate must be responsible for the production of the cyclopropane **3** and for the formation of dichloroethylenes **2** with a high percentage of E isomer. In this common intermediate, the "carbene−olefin complex", the perturbations of the properties of the carbene moiety by the interactions with the olefin change the ratio *E*/*Z* drastically.

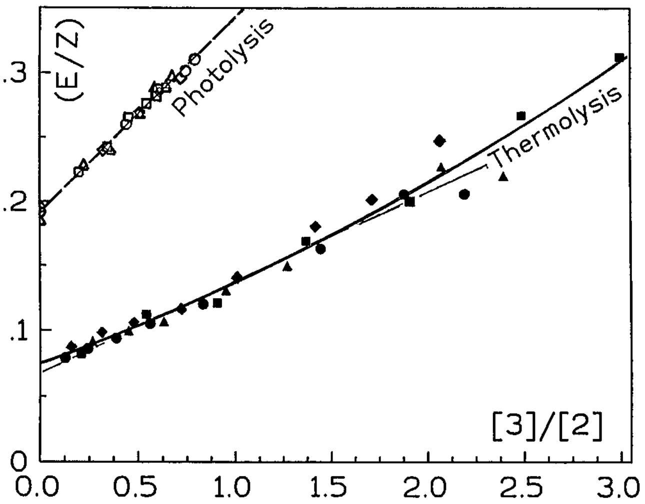
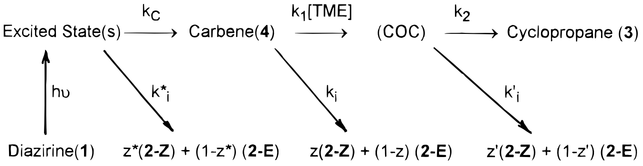


Figure 5. Relations between the values of the ratios [**2-E**]/[**2-Z**] and [**3**]/[**2**] for the system diazirine **1b** + TME under photolysis at 18 °C (○), 30 °C (◇), 45 °C (△), and 52 °C (□) and under thermolysis at 75 °C (■), 95 °C (◆), 102 °C (▲), and 110 °C(●).

Scheme 5



This effect may be analyzed quantitatively by using Scheme 5 and expressing the yield of formation of the cyclopropane, $\Phi_{(3)} = \alpha\{k_1[\mathrm{TME}]/(k_i + k_1[\mathrm{TME}])\}\beta$, and the yield of formation of **2-Z**, $\Phi_{(2-Z)} = (1 - \alpha)z^* + \alpha\{k_i/(k_i + k_1[\mathrm{TME}])\}z + \alpha\,(1-\beta)\{k_1[\mathrm{TME}]/(k_i + k_1[\mathrm{TME}])\}z'$ where the three terms correspond respectively to **2** produced by RIES, from the free carbene and from the COC. These two expressions yield $\Phi_{(2-Z)} = \alpha z + (1 - \alpha)z^* - \{z' + (z - z')/\beta\}\Phi_{(3)}$ under photolysis and $\Phi_{(2-Z)} = z - \{z' + (z - z')/\beta\}\Phi_{(3)}$ under thermolysis since then $\alpha = 1$.

The plots of [**2-Z**] *vs* [**3**] must therefore be straight lines for thermolysis and photolysis, and these lines should have the same slope. The values of [**2-Z**] and [**3**], obtained from the (**3**/**2**) and (**2-E**/**2-Z**) ratios by assuming that $\Phi_{(2)} + \Phi_{(3)} = 1$ and $\Phi_{(2)} = \Phi_{(2-Z)} + \Phi_{(2-E)}$, are plotted on Figure 6: the slopes are nearly identical (−0.954 (phot) and −0.990 (therm) and the very small difference, if significant, may be due to a small change of one (or several) of the parameters *z*, *z*′, and *β* with the temperature.

The slope of the line obtained from thermolysis, $-0.99 = -\{z' + (z - z')/\beta\}$ and the value $\beta = 0.85$ obtained from $([\mathbf{2}]/[\mathbf{3}])_\infty = 0.175$ yield $z' = 0.64$. Alternatively, the value of the *E*/*Z* ratio when [TME] → ∞, $(E/Z)_\infty \approx 0.70$ (obtained by nonlinear regression of *E*/*Z* *vs* [TME]), gives $z' \approx 0.59$ which, with the above expression of the slope, yields $\beta = 0.875$.

The behavior of the system $ClCH_2C(N_2)C$ + TME under photolysis and/or thermolysis on the temperature range 10−110 °C can be fully described by the set of parameters given in Table 5. For $CH_3(CH_2)_2C(N_2)Cl$, a similar analysis yields the data shown on the line 2 of the same table.

The *E*/*Z* ratio appears to be very sensitive to the nature of the species undergoing the rearrangement. We can use this sensitivity to determine the efficiency of the RIES process in benzylchlorodiazirines.This efficiency, found as very small from the analysis of the values of **2**/**3** or equal to 6% (±6%) from the PAC measurements, is in fact nonnegligible.

The plot of $(Z/E)_0$, the value of the ratio [**2-Z**]/[**2-E**] in the absence of olefin, as a function of the temperature for 3-

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

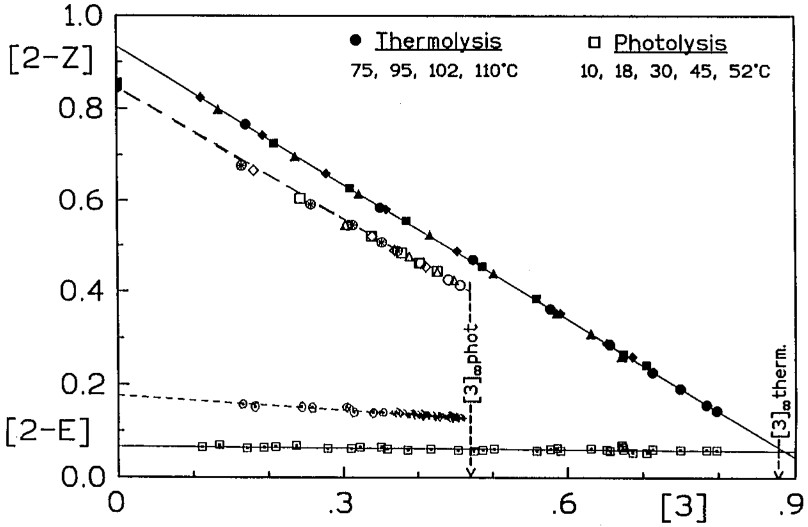

Figure 6. Relations between the relative amount of **2-Z**, i.e [**2-Z**]/([**2**] + [**3**]), and the relative amount of **3**, i.e [**3**]/([**2**] + [**3**]), produced by photolysis of the system diazirine **1b** + TME at 10 °C (○), 18 °C (△), 30 °C (□), 45 °C (◇) and 52 °C (⊗) and by thermolysis at 75 °C (●), 95 °C (■), 102 °C (◆), and 110 °C (▲). The relative amount of **2-E** is also shown with common symbols for the four thermolysis (○) and the five photolysis (□) data sets.

Table 5. Values of $\Phi_{(RIES)} = (1 - \alpha)$, $\Phi_{(COC\to 3)} = \beta$, and of the **2E:2Z** distributions for **2** Generated from RIES, Carbene, and COC (from data obtained by photolysis of several diazirines + TME)

TME + diazirine:	$\Phi_{(RIES)} = (1 - \alpha)$	**2-E**:**2-Z** (RIES)	**2-E**:**2-Z** (carbene)	$\Phi_{(COC\to 3)} = (\beta)$	**2-E**:**2-Z** (COC)
1b	0.52 ± 0.06	$\sim$25:75	6:94	0.85 ± 0.03	$\sim$40:60
1c	0.28 ± 0.05	$\sim$44:56	28:72	0.62 ± 0.03	$\sim$20:80[a]
1e	$\sim$0.05[b]	$\sim$50:50	$\sim$88:12 (90 °C)	$\sim$0.80	$\sim$78:22[c]
1f	$\sim$0.05[b]	$\sim$50:50	$\sim$89:11 (90 °C)	$\sim$0.80	$\sim$83:17[c]

[a] From photolytic data. [b] At 20 °C. [c] At 90 °C.

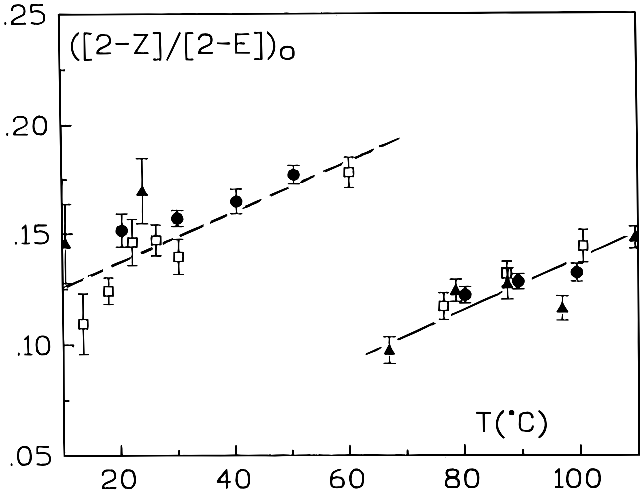

Figure 7. Variations, with the temperature, of the ratio [**2-Z**]/[**2-E**] for the decomposition of diazirines **1d** (▲), **1e** (□), and **1f** (●), by photolysis (below 60 °C) and by thermolysis (above 60 °C), in the absence of TME.

benzylchlorodiazirines, $XC_6H_4CH_2C(N_2)Cl$ with X = H, Cl, and Me, is given in Figure 7. The ratio $(Z/E)_0$ slightly increases with temperature as well under photolysis as under thermolysis, and for a given temperature, it is larger under photolysis than under thermolysis.

Under thermolysis at 60 °C for instance, $(Z/E)_0 \approx 0.10$, corresponding to a 91:9 distribution of the *E* and *Z* isomers, characteristic of the free carbene. Under photolysis, $(Z/E)_0 \approx 0.16$ (when extrapolated to the same temperature) corresponding to a 86:14 distribution; the relative amount of the *Z* isomer is thus nearly twice larger than under thermolysis. This can only be explained by assuming that, under photolysis, **2** is produced (i) from the free carbene with a 9:91 distribution, for a fraction (α) and (ii) by RIES, for a fraction $1 - \alpha$, with a much larger *Z*/*E* ratio.

The value $\alpha = 0.94$ given by the PAC measurements yield a 92:8 distribution of *Z* and *E* isomers for **2** produced by RIES, which does not seem quite reasonable; RIES is expected to give a distribution of isomers which is less selective than the rearrangement of the free carbene (as in the case of **1b** and **1c**); there seems to be no reason for RIES to produce the isomers of **2** with a large selectivity reversed with respect to that given by the free carbene! Assuming a distribution around 50:50 for the *Z* and *E* isomers of **2** produced by RIES, one gets $\alpha = 0.88$. Most probably, the real value of α at 60 °C is in the range of 0.80−0.95, i.e. $\alpha = 0.87 \pm 0.07$. With such a value, the shift between the lines "$\log(k_i/k_t)$ *vs* $1/T$" obtained under photolysis and thermolysis, as shown in Figure 4, would be only 0.06 which can easily escape observation. But a 10% efficiency for RIES should be detected on the plots of $([\mathbf{2}]/[\mathbf{3}])_\infty$ *vs* *T* such as those shown on Figure 8.

For the systems **1e** or **1f** + TME, when the values of $([\mathbf{2}]/[\mathbf{3}])_\infty$ are plotted *vs* *T* on an enlarged scale, the values obtained under thermolysis show a large scatter, but they are more or less independent of the temperature whereas those obtained under photolysis show a clear tendency to increase with temperature and are significantly larger than the former when extrapolated to the range of temperatures used for thermolysis. In the case of "**1e** + TME" for instance, the ratio $([\mathbf{2}]/[\mathbf{3}])_\infty$ is around 0.25 under thermolysis (76−100 °C) whereas it is $\sim$0.28 at 13.5 °C, 0.33 at 30 °C, and 0.375 at 60 °C under photolysis. With $[\mathbf{2}]_\infty = (1 - \alpha) + \alpha(1 - \beta)$ and $\beta = 0.8$, these values of $([\mathbf{2}]/[\mathbf{3}])_\infty$ yield $\alpha = 0.97$ at 13 °C, 0.94 at 30 °C, and 0.90 at 60 °C, in good agreement with $\alpha = 0.94$ at 30 °C, obtained from PAC measurements, and $\alpha = 0.88$ at 60 °C found above from the ratio *Z*/*E* by assuming that RIES gives a 50:50 distribution for **2-Z**:**2-E**. Therefore it seems that, for benzyl-

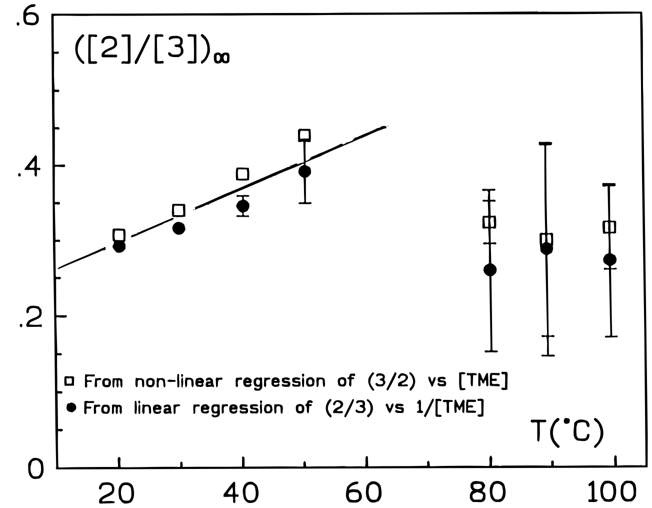

Figure 8. Temperature dependence of the ratio [**2**]/[**3**] when [TME] → ∞ for diazirine **1f** under photolysis ($T < 60$ °C) and thermolysis ($T > 60$ °C): (●) from intercepts of linear plots of [**2**]/[**3**] *vs* 1/[TME] and (□) from nonlinear regression of [**3**]/[**2**] *vs* [TME].

chlorodiazirines, the efficiency of the RIES process increases with temperature.

It may be noted that this temperature dependence of the efficiency of the RIES process is not observed with $ClCH_2C(N_2)Cl$: the values of ([**2**]/[**3**])$_\infty$ obtained under photolysis are remarkably constant over the whole temperature range 0−50 °C. This may be explained by the fact that, in the case of **1b**, the rates for RIES and for carbene formation are similar ($\alpha \approx 0.5$), so that these two processes which most probably originate from the same excited state of the diazirine must have similar temperature dependence.

For the system "**1f** + TME" under thermolysis, the plots of [**2-E**] and [**2-Z**] *vs* [**3**] give straight lines with the following equations: [**2-E**] = 0.886 − 0.899[**3**] and [**2-Z**] = 0.114 − 0.101[**3**]. The values of [**2-E**] and [**2-Z**], calculated with [**3**] = 0 and [**3**] = [**3**]$_\infty$ = 0.8, yield respectively $(E/Z)_{\mathrm{carb}} = 7.77$ and $(E/Z)_{\mathrm{COC}} = 5.0$. Similar values are obtained for the system **1e** + TME, as shown in Table 5.

The overall *E*/*Z* ratio measured under thermolysis changes little when [TME] increases, because the *E*:*Z* distribution for **2** produced from the carbene and from the COC are similar, whereas the small amount of RIES, increasing with temperature, is sufficient to modify noticeably the *E*/*Z* ratio measured under photolysis because the *E*:*Z* distribution for **2** produced by RIES is quite different. This clearly appears on the plots of [**2-E**] and [**2-Z**] *vs* [**3**], in Figure 9, where the amount of [**2-Z**] obtained under photolysis is always ~4% higher than under thermolysis, whatever the amount of **3** is, i.e. whatever the concentration of TME is. These 4% represent in a first approximation the amount of **2-Z** produced by RIES with an efficiency ~50% whereas both the free carbene and the COC produce mainly the **2-E** isomer.

Conclusion

The features explained by a COC such as the branching ratios ([**2**]/[**3**]) and (**2-E**/**2-Z**) could also be rationalized by assuming that there are two types of "encounter complexes" between a carbene and an olefin, one giving only (**2** + olefin) and the other producing only the cyclopropane **3**. However it seems reasonable and economical to assume that there is only one type of encounter complex.

A diazo compound could also explain the data if it yields **2** directly (i.e. without formation of carbene) and can react with olefins to yield ultimately **3** after N_2 loss. However, as stated in the Introduction, the yield of formation of such diazo intermediate from chlorodiazirines at ambient temperatures is very small and the yield of **2** produced in this manner must be even smaller. We are confident that this pathway alone cannot account for the amount of **2** predicted to be produced in thermolysis of solutions where the concentration of olefin would be infinite, i.e. *ca.* 15% for **1b**, *ca.* 20% for **1d**−**f** or nearly 40% for **1c**. Our results certainly do not prove the existence of COC, but this elusive species can best explain the data.

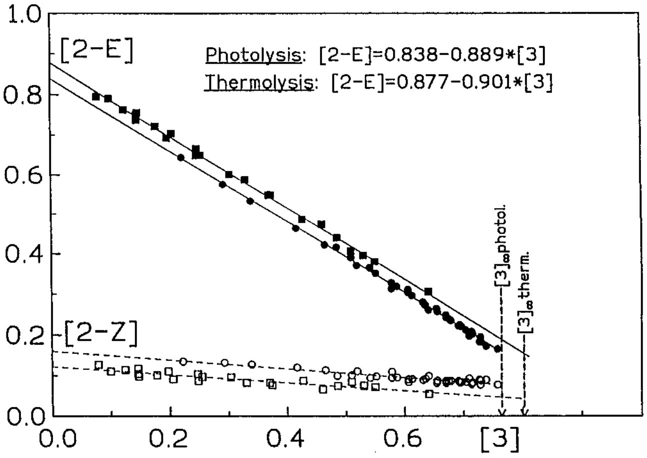

Figure 9. Relations between the relative amounts of **2-Z** (● and ■) and **2-E** (○ and □) and the relative amount of **3** produced by photolysis (□ and ■, 4 temperatures) and by thermolysis (○ and ●, three temperatures) of the system diazirine **1e** + TME.

Recently, Moss[1a] stated "*... there are two presently unsolved questions that temper our conclusions. These are (1) the possible intervention of carbene/alkene complexes, and (2) the extent of carbene-mimetic reactions that occur via the excited states of the carbene precursors...*". The choice between these two alternatives has been a matter of much controversy. Our present experimental results provide evidence that both mechanisms, COC and RIES, are operating, but with relative efficiencies depending on the system studied.

The efficiency of the RIES process, Φ_{RIES}, has been previously examined and correlated to the α-CH bond dissociation energy;[1b,6b] the stronger the α-CH bond, the greater yield of carbene, and presumably the lower the RIES efficiency. The relative yields for carbene formation from a series of alkylchlorodiazirines, estimated from the amplitude of the pyridinium ylide absorption, were found to be 1, 0.52, 0.38, 0.29, and 0.02 when the alkyl group is cyclopropyl or *tert*-butyl, methyl, benzyl, ethyl, and isopropyl, respectively. Since the quantum efficiency for carbene formation from *tert*-butylchlorodiazirine was measured[3b] to be ~0.90, these yields correspond to Φ_{RIES} values of 0.10, 0.53, 0.66, 0.74, and 0.98. The general trend shown by these numbers does correlate with the α-CH bond dissociation energy, but the absolute values are not in good agreement with those given herein. For methyl- and benzylchlorodiazirines, PAC measurements and product analysis gives Φ_{RIES} values less than 0.33 and 0.05, respectively, significantly less than those observed by the ylide trapping method. In addition, experiments on chloromethyl- and propylchlorodiazirines suggest lower values for Φ_{RIES} than obtained by the ylide method. The reason for these discrepancies is not immediately apparent[16,17] but it seems that the relation between Φ_{RIES} and the dissociation energy of the α-CH bond should be considered with care.

The efficiency of the carbene rearrangement, $\Phi_{\mathrm{COC}\rightarrow 2} = 1 - \beta$, can be obtained by substracting Φ_{RIES} from the yield of rearranged product, $\Phi_{\mathbf{2}\infty}$, which is obtained from the ratio $([\mathbf{2}]/[\mathbf{3}])_\infty$. It seems difficult to propose a relation between this efficiency and the nature of both the carbene and the olefin since there are only a few relevant available data. For TME and methylchlorocarbene, $\Phi_{COC\rightarrow 2} = 0.09$ using $\Phi_{RIES} = 0.24$ and $([\mathbf{2}]:[\mathbf{3}])_\infty = 67:33$.[3a] This value is similar to those found for alkylchlorocarbenes **1b**, **1d**, **1e**, and **1f** with the same olefin which have $\Phi_{COC\rightarrow 2}$ values around 0.2.

The $\Phi_{COC\rightarrow 2}$ values for benzylchlorocarbene and various olefins, calculated by using previously published data,[9a] are given in Table 6. No apparent correlation is found between $\Phi_{COC\rightarrow 2}$ and the rate constant of trapping of the carbene by the olefin or between $\Phi_{COC\rightarrow 2}$ and the "π-molecular electronegativity" of the olefin. Most of the olefins, including very reactive TME, unreactive 1-hexene, electron deficient chloroacrylonitrile, and electron rich TME give $\Phi_{COC\rightarrow 2}$ around 0.2 or 0.3. However, olefins diethyl fumarate and diethyl mesaconate have high $\Phi_{COC\rightarrow 2}$ values: 0.62 and 0.71, respectively. The reason for these large values is not obvious, but might be due to the interaction of the electrophilic carbene with the ester groups which does not lead to product but rather to rearrangement or, more probably, to a steric effect of the two ethyl ester substituents in a *trans* position on the double bond. This steric factor would not affect the rate constant for trapping of the carbene by the olefin (i.e. the rate constant of formation of the COC) if the carbene−olefin distance is *relatively long* in the COC, but it might be quite decisive when the carbene−olefin distance must be strongly reduced to form the cyclopropane adduct.

Table 6.[a] Yields of **2** Generated from the COC, $\Phi_{COC\rightarrow 2}$, Calculated from the Ratio $[\mathbf{2}]/[\mathbf{3}]_\infty$, in the Photolysis of Diazirine **1d** in the Presence of Various Olefins

olefin	TME	BVE	HEX	MES	DEF	Cl-ACN
$[\mathbf{2}]/[\mathbf{3}]_\infty$	0.30	0.44	0.52	3.15	2.0	0.64
[**2**]	23%	30%	34%	76%	67%	39%
$\Phi_{COC\rightarrow 2}$	0.18	0.25	0.29	0.71	0.62	0.34

[a] $\Phi_{\mathbf{2}\text{-COC}}$ calculated with $\Phi_{RIES} = 0.05$ at 25 °C: BVE, *n*-butyl vinyl ether; HEX, 1-hexene; MES, diethyl mesaconate; DEF, diethyl fumarate; Cl-ACN, α-chloroacrylonitrile.

Supporting Information Available: Details of the synthesis of diazirines, irradiation and product analysis, and product studies (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(16) In fact, in the Figure 3 of ref 6b, White and Platz use a "normalized" value of the ylide absorption which greatly improves the correlation between the yield of carbene formation and the dissociation energy of the α-CH bond. Normalization is "justified" by expected change in the value of the absorption coefficient between pyridinium ylides of benzylchlorocarbene and other alkylchlorocarbenes, but this yields an even more unrealistic value of the quantum yield of carbene formation, ~4%!

(17) The pyridine ylide method relies on the assumption that, when [pyridine] is large enough, i.e. ~1−5 M, every carbene produced is trapped by the pyridine. This is justified when the carbene lifetime is longer than a few nanoseconds since the rate constant for ylide formation, k_{yl}, is usually in the range $(1-5) \times 10^9$ M^{-1} s^{-1}. This may be unjustified for carbenes with a lifetime around or shorter than a nanosecond, especially if substituent(s) increasing the rate of the 1,2-H shift also decrease the value of k_{yl} by increasing the electron density on the carbene center.