Energy Barrier for 1,2-Hydrogen Migration in Benzylchlorocarbene

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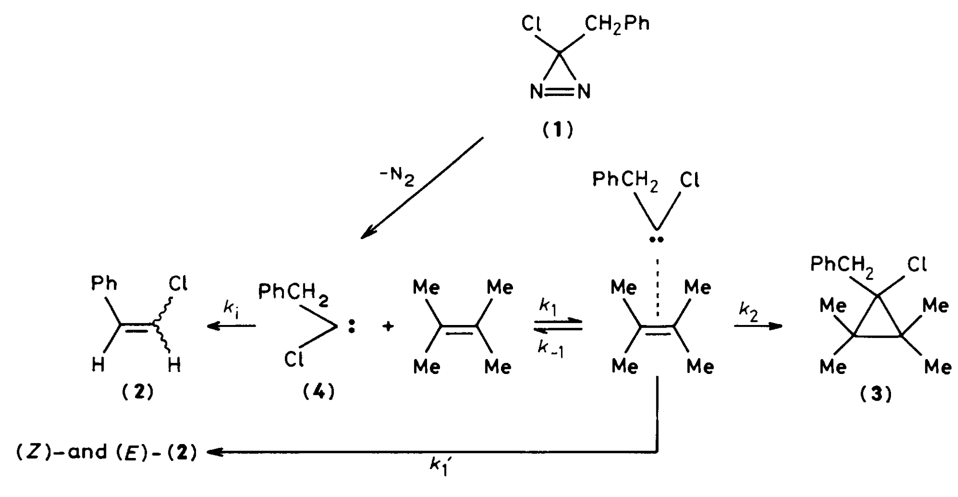
The intermolecular–intramolecular rate constants derived from the thermolysis and photolysis of 3-chloro-3-benzyldiazirine in tetramethylethylene gave an excellent Arrhenius plot; an activation energy of 6.4 kcal mol^{-1} (26.8 kJ mol^{-1}) was obtained for the 1,2-H migration in benzylchlorocarbene.

Intramolecular reactions involving 1,2-hydrogen shifts to a divalent carbon have been observed.[1—3] While the energy barrier for this rearrangement has been the subject of numerous theoretical investigations,[2,4] only recently has an experimental estimate been reported of the activation barrier for the vinylidene–acetylene rearrangement.[5] This is consist-



Scheme 1

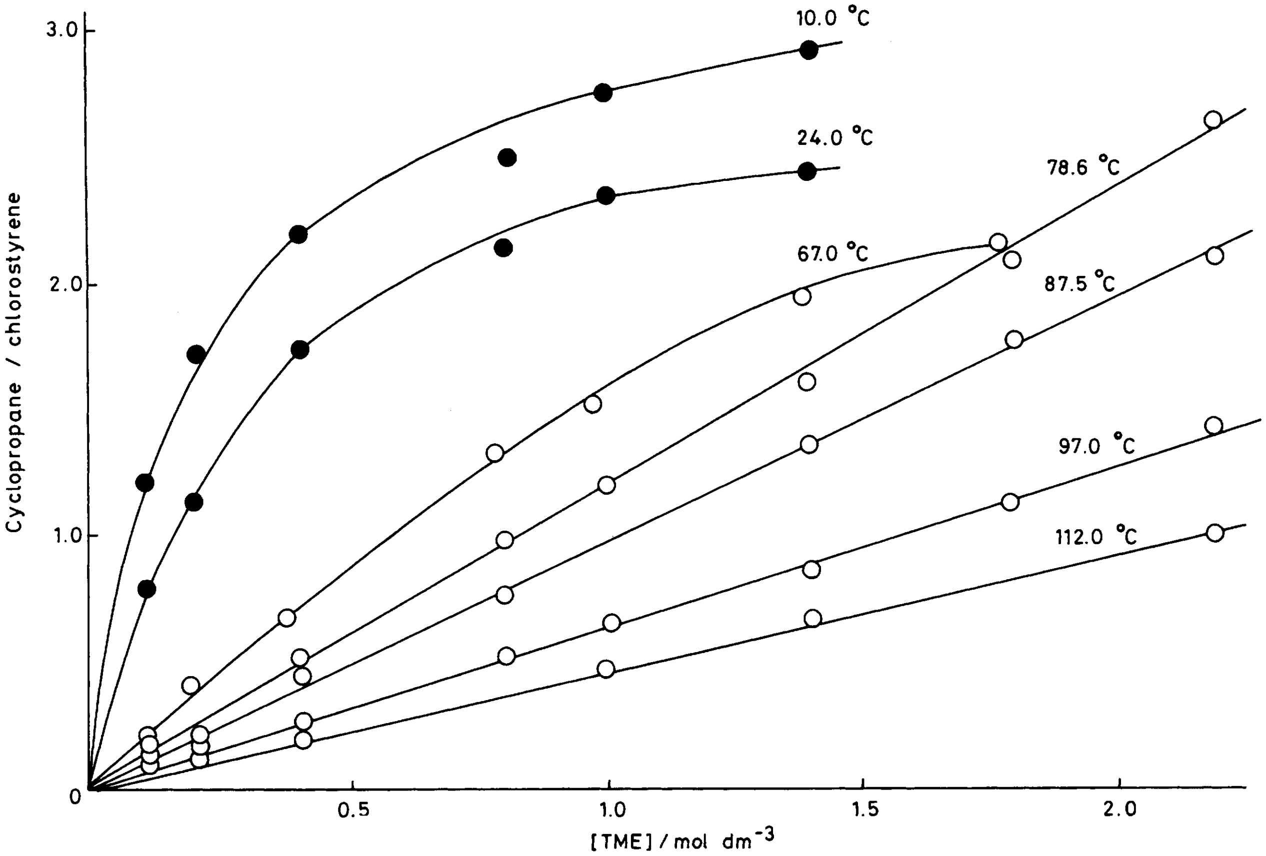


Figure 1. Plots of cyclopropane/chlorostyrene *vs.* [TME]; ● photolysis, ○ thermolysis.

Table 1. Product distribution in the photolysis and thermolysis of (**1**) in TME.

[TME]/ mol dm^{-3}	*hν* 10.0 °C		*hν* 24.0 °C		67.0 °C		78.6 °C		87.5 °C		97.0 °C		112.0 °C	
	(*Z*)-(**2**)/ (*E*)-(**2**)	(**3**)/(**2**)	(*Z*)-(**2**)/ (*E*)-(**2**)	(**3**)/(**2**)	(*Z*)-(**2**)/ (*E*)-(**2**)	(**3**)/(**2**)	(*Z*)-(**2**)/ (*E*)-(**2**)	(**3**)/(**2**)	(*Z*)-(**2**)/ (*E*)-(**2**)	(**3**)/(**2**)	(*Z*)-(**2**)/ (*E*)-(**2**)	(**3**)/(**2**)	(*Z*)-(**2**)/ (*E*)-(**2**)	(**3**)/(**2**)
0.1	0.37	1.20	0.32	0.776	0.11	0.19	0.12	0.145	0.12	0.110	0.12	0.0848	—	—
0.2	0.46	1.70	0.47	1.14	0.11	0.39	—	—	0.13	0.200	0.11	0.159	0.15	0.0821
0.4	0.54	2.17	0.52	1.72	0.12	0.68	0.13	0.520	0.13	0.445	0.14	0.294	0.15	0.182
0.8	0.68	2.48	0.64	2.13	0.14	1.31	0.13	0.980	0.15	0.740	0.14	0.503	—	—
1.0	0.62	2.73	0.60	2.36	0.15	1.52	0.14	1.18	—	—	0.14	0.636	0.15	0.450
1.4	0.66	2.90	0.67	2.41	0.18	1.92	0.14	1.58	0.16	1.33	0.15	0.810	0.16	0.658
1.8	—	—	—	—	0.22	2.10	0.14	2.05	0.15	1.76	0.16	1.09	—	—
2.2	—	—	—	—	—	—	0.14	2.62	0.15	2.07	0.17	1.41	0.16	0.991
	$\frac{k_t}{k_i} = 19.34 \pm 0.60$		$\frac{k_t}{k_i} = 10.35 \pm 0.40$		$\frac{k_t}{k_i} = 1.98 \pm 0.020$		$\frac{k_c}{k_i} = 1.15 \pm 0.026$		$\frac{k_c}{k_i} = 0.977 \pm 0.021$		$\frac{k_c}{k_i} = 0.604 \pm 0.018$		$\frac{k_c}{k_i} = 0.456 \pm 0.009$	

ent with the observations[6—8] of substituent effects for 1,2-H migration in a carbene. We report here the results of our studies on the energy barrier for a 1,2-H shift in benzylchlorocarbene.

3-Chloro-3-benzyldiazirine (**1**) was synthesized by Grahams method[9] and 0.020 M solutions of (**1**) in iso-octane were photolysed† at 10 and 24 °C in the presence of various amounts of tetramethylethylene (TME, 0.1—1.4 M) so that there was always an excess of alkene. The products of the reaction were (*E*)- and (*Z*)-chlorostyrenes (**2**) and 1-benzyl-1-chloro-2,2,3,3-tetramethylcyclopropane (**3**).‡ The results are given in Table 1 and displayed in Figure 1. Plots of (**3**)/(**2**) *vs.* [TME] show pronounced curvature which suggest the formation of an

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† Note that irradiation of (**1**) at 4 K produced no detectable e.s.r. signal. We are grateful to Dr. K. F. Preston for carrying out these experiments. Addition of benzylchlorocarbene to (*Z*)-4-methylpent-2-ene was stereospecific.[10] It is believed that this carbene is reacting in its singlet ground state. Halogenocarbenes generated from photolysis of halogenodiazirenes are known to have singlet ground states.[11]

‡ Products (**2**) and (**3**) were identified by n.m.r. and mass spectroscopic analysis. Relative yields of products were analysed on a Varian VISTA 6000 g.c. using an 8 ft column packed with 5% Carbowax 20M on Chromosorb. Peak areas were integrated on a HP3390A recorder. The peak area ratio of (**2**)/(**3**) was converted into mole ratio by multiplying a response factor of 1.47. Product balance shows that 90% of (**1**) could be accounted for in terms of (**2**) and (**3**).

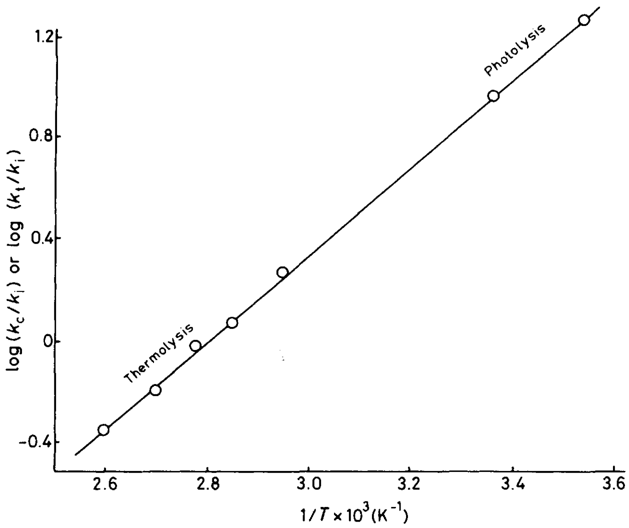


Figure 2. Arrhenius plot of k_c/k_i and k_t/k_i.

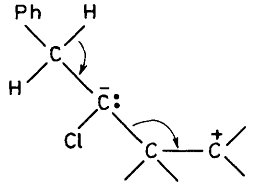
intermediate prior to cyclopropane formation. A reversibly formed adduct of this type has been postulated by Turro and Moss[12] for the reaction of $\mathrm{Ph{-}\ddot{C}{-}Cl}$ with TME. To account for the observed results, a mechanism is proposed (Scheme 1) in which two parallel routes to (**2**) are operative.§

Application of steady-state treatment to the scheme leads to the expresson given in equation 1, where the overall trapping rate constant, k_t, is equal to $k_1k_2/(k_{-1} + k_2 + k_i')$. The ratio (**2**)/(**3**) has an inverse first-order dependence on TME. A least-squares analysis of the data in Table 1 gives the values k_t/k_i with the error limits quoted as standard deviations.

$$\frac{(\mathbf{2})}{(\mathbf{3})} = \frac{k_i'}{k_2} + \frac{k_i}{k_t}\frac{1}{[\mathrm{TME}]} \qquad (1)$$

The thermal decomposition of (**1**) (0.020 M in iso-octane) in various concentrations of TME was carried out to 10 half-lives and product ratios were determined at four temperatures. The ratios for (**3**)/(**2**) *vs.* [TME] from Table 1 are plotted in Figure 1. The curvatures which had been noted in the photolysis experiments were not observed and instead straight lines were obtained for all the thermolysis experiments (>78 °C). The values for k_c/k_i can be obtained (Table 1) from the slopes of the linear plots in Figure 1 where k_c is the rate constant for cyclopropanation. A plot of log (k_c/k_i) and log (k_t/k_i) *vs.* $1/T$ is shown in Figure 2. It can be seen that both sets of data, when applied to an Arrhenius plot, fall on the same straight line. This represents very convincing evidence that the reaction in thermal systems is the same as that of the photolysis experiments, and that k_t must be identical to k_c at temperatures above 10—110 °C. The thermolysis results at 67 °C show a curve for (**3**)/(**2**) *vs.* [TME]. Least-squares analysis of (**2**)/(**3**) *vs.* 1/[TME] gives a value of 1.98 for k_t/k_i; this correlates well with the Arrhenius plots in Figure 2. A mechanism involving an excited carbene has been postulated by Warner[13] for some of our previous results.[10] However, the co-linearity of the Arrhenius plots suggests that the carbene, (**4**), which is generated photochemically, does not react in its excited state.

Recall that $k_t = k_1k_2/(k_{-1} + k_2 + k_i')$. At 10 °C, as Turro and Moss have shown, $k_{-1} \gg k_2$ for the addition of $\mathrm{Ph{-}\ddot{C}{-}Cl}$ to TME. The values for k_i'/k_2 at 10 and 24 °C can be evaluated from the intercept of equation 1 and are found to be



(I)

approximately equal to 0.3, therefore, k_t becomes k_1k_2/k_{-1} or Kk_2. Since the photochemical and thermal data have the same Arrhenius activaton energy, the value of k_c must be equal to k_1k_2/k_{-1} as well. Had the equation $k_t = k_1k_2/(k_{-1} + k_2 + k_i')$ not been reduced to Kk_2, the Arrhenius law could not have applied. The slope of the plot in Figure 2 has a value of 1.77×10^3 K; hence $E_t - E_i = -8.10 \pm 0.17$ kcal mol^{-1}.¶ If the activation energy for the cyclopropanation is taken as -1.7 kcal mol^{-1},[12] then a value of 6.4 kcal mol^{-1} is obtained for the 1,2-H shift in chlorobenzylcarbene. From the intercept ($A_t/A_i = 1.26 \times 10^{-5}$) and the recent value of A_t (1.9×10^7 dm^3 mol^{-1} s^{-1}) from Turro and Moss,[12] the frequency factor for the 1,2-H shift (A_i) can be calculated to be 1.5×10^{12} dm^3 mol^{-1} s^{-1}.

To our knowledge there are no experimental data reported on the activation energy for 1,2-H migration in a carbene except the recent estimate of *ca.* 12 kcal mol^{-1} deduced for the activation barrier for the vinylidene–acetylene rearrangement.[5] It is generally accepted that 1,2-H shifts occur with essentially zero activation energies[2,4a,b] since these reactions are thought to proceed very rapidly. The observation of substituent effects for 1,2-H migration in carbenes[6—8] implies an activation energy; the present finding for $E_a = 6.4$ kcal mol^{-1} provides evidence for the existence of a barrier in 1,2-H migration.

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§ The decomposition of the adduct to give chlorostyrene may be viewed as a 1,4-*anti*-elimination, see (I).

¶ 1 cal = 4.18 J.