

## Energy Barrier for 1,2-Chlorine Migration in $\alpha$ -Methyl- $\alpha$ -chlorobenzyl(chloro)carbene

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An activation energy of 3.4 kcal mol<sup>-1</sup> (1 cal = 4.184 J) was obtained for the 1,2-chlorine migration in  $\alpha$ -methyl- $\alpha$ -chlorobenzyl(chloro)carbene.

Recently, we reported the absolute rate constants and the activation energy for 1,2-hydrogen migration in benzyl(chloro)carbene<sup>1</sup> to  $\beta$ -chlorostyrenes ( $E_a = 4.8 \pm 0.2$  kcal mol<sup>-1</sup>; 1 cal = 4.184 J). This is in excellent accord with the experimentally determined value<sup>2</sup> of 6.4 kcal mol<sup>-1</sup>. We now

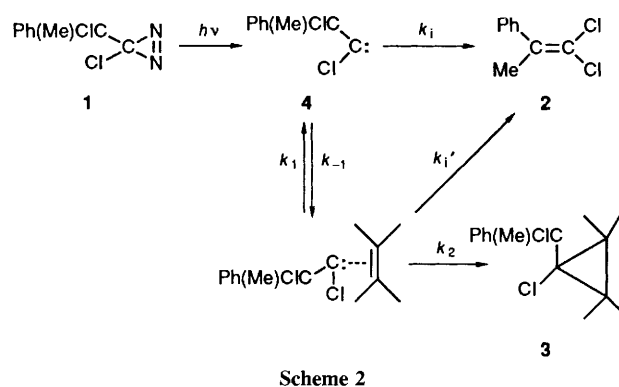
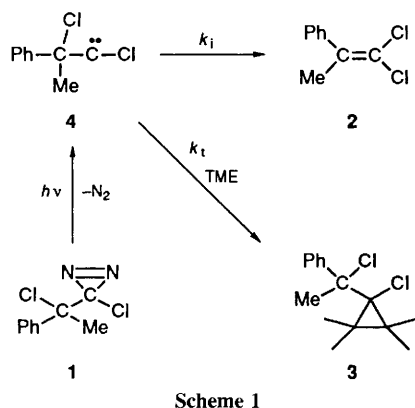
report the first determination of the activation energy for 1,2-chlorine migration in  $\alpha$ -methyl- $\alpha$ -chlorobenzyl(chloro)carbene **4**.

3- $\alpha$ -Methyl- $\alpha$ -chlorobenzyl-3-chlorodiazirine **1** [IR,  $\nu_{\max}$  1560 cm<sup>-1</sup>; UV (hexane),  $\lambda_{\max}/\text{nm}$  363 ( $\epsilon$  21), 353 (41), 347

**Table 1** Product distribution in the photolysis of **1** in TME at different temperatures

[TME]/dm <sup>3</sup> mol <sup>-1</sup>	Cyclopropane, <b>3</b> /styrene, <b>2</b>				
	-12.5 °C	1.0 °C	10.2 °C	18.6 °C	24.8 °C
0.795	0.397	0.204	0.133	0.098	0.0794
1.59	0.537	0.294	0.192	0.146	0.131
3.18	0.694	0.384	0.274	0.211	0.178
4.77	0.680	0.408	0.289	0.240	0.217
6.36	0.730	0.515	0.327	0.255	0.216
7.95	0.725	0.543	0.370	0.296	0.225
<i>k<sub>i</sub>/k<sub>t</sub></i> <sup>a</sup>	1.03 ± 0.060	2.60 ± 0.18	4.12 ± 0.19	5.78 ± 0.28	7.26 ± 0.23

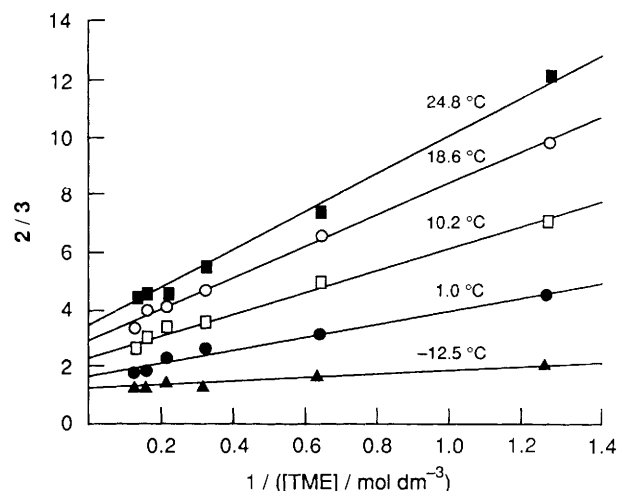
<sup>a</sup> Error limits are quoted as standard deviations.



(50), 343 (50) and 336 (50)] was synthesized by the oxidation of the corresponding amidine using sodium hypochlorite.<sup>3</sup> Irradiation of the diazirine **1** (350 nm) in isooctane resulted in the formation of nitrogen and  $\alpha$ -methyl- $\beta$ -dichlorostyrene **2**, Scheme 1. In the presence of tetramethylethylene (TME), the cycloadduct **3** was also formed in competition with the intramolecular 1,2-chlorine shift to form **2**. Addition of  $\alpha$ -methyl- $\alpha$ -chlorobenzyl(chloro)carbene **4**, to *Z*-4-methylpent-2-ene is stereospecific indicating that carbene **4** is reacting in its singlet ground state. Products of reaction were isolated by column chromatography and identified through NMR and mass spectrometry. The product distributions were determined by gas chromatography.

Photolysis of the diazirine **1** (0.06 mol dm<sup>-3</sup>) in isooctane in the presence of various concentrations of TME (1–8 mol dm<sup>-3</sup>) over the temperature range -12 to 25 °C yielded the results in Table 1. † Plots of **3/2** vs [TME] show pronounced curvature. Such curvature has been observed for other benzylhalocarbenes and interpreted in terms of an additional pathway to the formation of styrenes involving carbene-alkene complexes,<sup>1,2</sup> excited carbenes<sup>4</sup> or diazo compounds.<sup>5</sup> Regardless of the nature of intermediate, the kinetics lead to similar analytical expressions.<sup>6</sup> We favour the carbene-alkene complex here (Scheme 2) because it predicts an intercept which depends on the nature of the alkene substrate as demonstrated earlier.<sup>1</sup>

† Note added in proof. The photolysis of **1** in isooctane gave 90% of *Z* ( $\delta_{Me} = 2.19$ ) and 10% of *E* ( $\delta_{Me} = 2.40$ ) 1,2-dichloro-1-phenyl-1-propene in a 2:1 ratio. Intramolecular 1,3-C-H insertion is absent. Migration of Cl is preferred to that of methyl or phenyl by a factor of 9.



**Fig. 1** Relative proportions of the styrene **2** and cyclopropane **3** vs.  $1/[TME]$  at different temperatures in the photolysis of the diazirine **1**

Application of steady-state treatment to Scheme 2 leads to expression (1) where the overall cyclopropanation rate constant,  $k_t$ , is equal to  $k_1 k_2 / (k_{-1} + k_2 + k_i')$ . The ratio **2/3** has an inverse first-order dependence on TME concentrations, Fig. 1. Least-squares analysis of the data gives the values for  $k_i/k_t$  in Table 1.

$$\frac{2}{3} = k_i'/k_2 + k_i/(k_t[TME]) \quad (1)$$

The Arrhenius plot for these values ( $\log k_i/k_t$  vs.  $1/T$ ) gives  $E_i - E_t = 8.08 \pm 0.40$  kcal mol<sup>-1</sup> and  $\log_{10} (A_i/A_t) = 6.82 \pm 0.32$ . If the activation energy and *A* factor for the cyclo-

propanation of **4** with TME are taken to be the same as found for *p*-chlorobenzyl(chloro)carbene,<sup>7</sup> then the kinetic parameters for 1,2-chlorine shift in the carbene **4** can be calculated [eqn. (2)]. Thus, the lifetime ( $\tau = 1/k_i$ ) for carbene **4** can be calculated to be  $< ca. 1$  ns at room temperature.

$$k_i = 10^{12.1} \exp(-3.40 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1} \quad (2)$$

Laser flash photolysis of 3-benzyl-3-chlorodiazirine in isooctane produces benzyl(chloro)carbene which reacts with pyridine to form an ylide or undergoes 1,2-H migration to form *Z*- and *E*- $\beta$ -chlorostyrenes. The rate for 1,2-H migration is determined by plotting the pseudo-first-order rate constants for the growth of the ylide *vs.* [pyridine] and extrapolating to zero pyridine concentration.<sup>1</sup> In  $\alpha$ -methylbenzyl(chloro)carbene the 1,2-H migration is so fast that the determination of  $k_i$  by the above method is beyond the capability of nanosecond laser spectroscopy. In this case only the ratio  $k_y/k_i = 13$  ( $k_y$  is the rate constant for reaction of carbene with pyridine) has been determined.<sup>8</sup> Assuming that  $k_y$  is very similar for alkylhalocarbenes and close to  $9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , the lifetime for  $\alpha$ -methylbenzyl(chloro)carbene can be calculated to be approximately equal to 1 ns. In this respect, the 1,2-H shift and 1,2-Cl shift in benzylchlorocarbenes are

similar suggesting that the size of the migrating atom has no dramatic effect on the rates. Finally, we have demonstrated that the relative rate technique is a powerful method to get an estimate of  $E_a$  for 1,2-shift even under conditions where ns laser spectroscopy encounters difficulties.

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