

SHORT COMMUNICATION

FIRST DETERMINATION OF AN ABSOLUTE RATE CONSTANT FOR A 1,2-PHENYL MIGRATION TO A CARBENE

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*Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, C1A 4P3, Canada***The first determination of a 1,2-phenyl shift in α,α -dimethylbenzylchlorocarbene was achieved by nanosecond laser flash photolysis, $\tau = 50$ ns.**

The absolute rates for the intramolecular 1,2-H, 1,2-CH₃ and 1,2-Cl migrations to a carbene center, affording an alkene, have been a subject of intensive study by laser flash photolysis (LFP)¹ and these investigations have been reviewed recently.² Theoretical calculations of activation energies for 1,2-H shifts in singlet carbenes have been carried out using MP4/6–311G** energies calculated on MP2/6–31G* optimized geometries.³ There is a general agreement between theory and experiment that the rate of migration is a function of the substituent on the carbene; the observed activation barriers are usually several kcal mol⁻¹.

The competitive 1,2-phenyl, 1,2-methyl and 1,2-hydrogen migrations in carbenes have been observed by product analysis.⁴ The migratory aptitude⁵ is given as H > Ph > CH₃. However, the absolute rate for a 1,2-phenyl shift to a carbene has never been measured experimentally.

We now report the LFP of 3-chloro-3-(α,α -dimethylbenzyl)diazirine (**1**). The results obtained led to the first determination of a rate constant for a 1,2-phenyl shift in (α,α -dimethylbenzyl) chlorocarbene (**2**). The chemistry of carbene **2** is unique in that the carbene undergoes 1,2-phenyl migration exclusively; no 1,2-methyl migration was found to occur at room temperature.

The LFP apparatus uses a crossed-beam arrangement. A mode-locked Nd:YAG laser (*ca* 10 mJ, pulse width 200 ps) provided excitation at 355 nm with a pulsed xenon lamp as the monitoring source. The system has a response time of 2 ns. All data collected are signal averaged over ten shots.

The diazirine **1** was prepared by the oxidation of the

α,α -dimethylbenzylamidine according to Graham's method⁶ (yield *ca* 5%) and purified by chromatography on silica gel. IR (N=N), 1573 cm⁻¹; UV, λ (MeOH) 340 ($\epsilon = 63$), 360 ($\epsilon = 61$); NMR, δ 7.32 (br s, 5H), 1.50 (s, 6H).

Photolysis (350 nm) of a 0.1 M solution of **1** in hexane for 5 h at 25 °C produced α -chloro- β,β -dimethylstyrene (**3**) as the only product (yield 90%). NMR (CDCl₃), δ 1.73 (s, 3H), 2.00 (s, 3H) and 7.30 (br s, 5H); ¹³C NMR (CDCl₃), δ 21.8, 22.0, 125.5, 127.6, 128.1, 129.2, 130.3 and 139.6; MS, *m/z* 168 (21), 166 (63), 131 (100). No azine was detected. Cyclopropane was not detected even with a ten-fold excess of tetramethylethylene, probably owing to steric hindrance. LFP of **1** (0.1 M) in isooctane does not produce a transient signal owing to the absorption of carbene **2**. However, LFP of **1** in the presence of pyridine produces a transient species with an absorption band peaking at around 360 nm. This transient is not present in the absence of pyridine and is attributed to pyridinium ylide (**4**).

The rate of formation of this ylide allows the determination of the absolute rate constant for the 1,2-phenyl migration in carbene **2**. A plot of the observed pseudo-first-order rate constants (25 °C) for the increase in absorption at 380 nm vs pyridine concentration is linear (Figure 1). The slope gives the rate constant for the reaction of carbene with pyridine, $k_y = 4.5 \pm 0.2 \times 10^9$ l mol⁻¹ s⁻¹ and the intercept (extrapolation to [pyridine] = 0) yields the rate constant for the 1,2-phenyl shift, $k_1 = 2.0 \pm 0.2 \times 10^7$ s⁻¹.

Strictly, the intercept in Figure 1 is equal to k_1 , the rate constant representing the sum of all first-order and

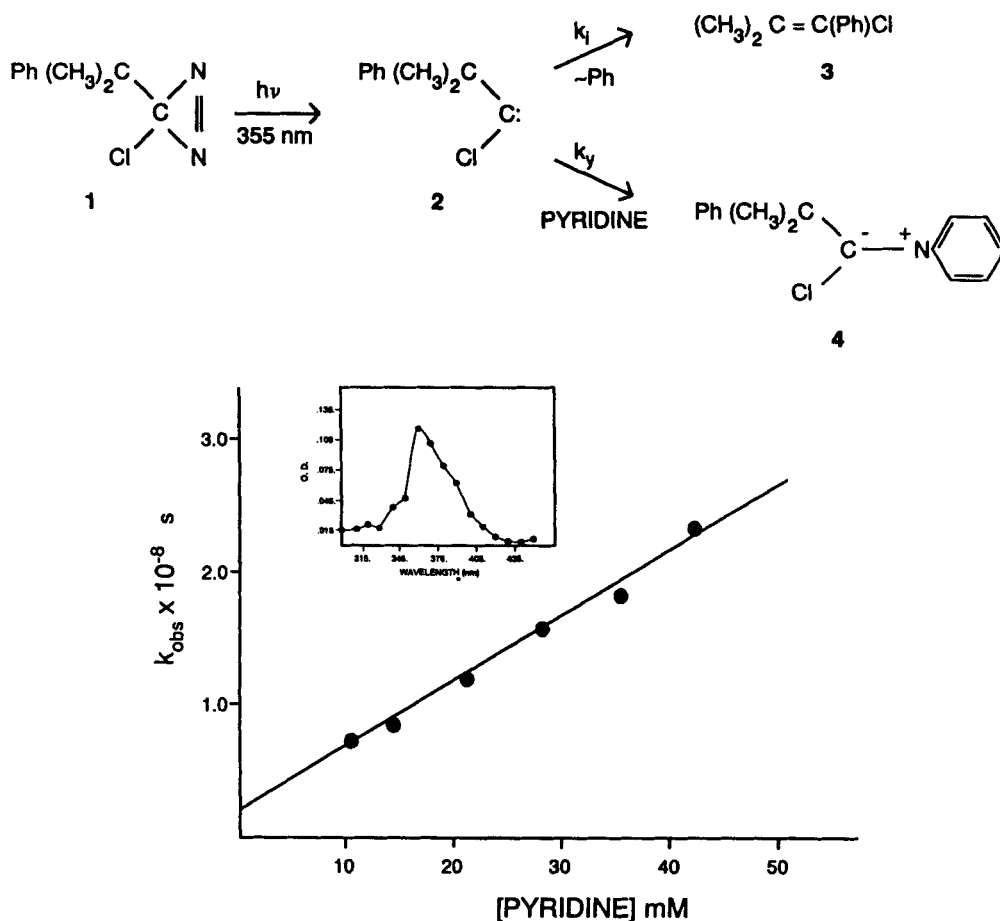


Figure 1. Plot of observed pseudo-first-order rate constants for increase in pyridinium ylide at 380 nm vs pyridine concentration at 25 °C. Inset: transient absorption spectrum of ylide 4 produced by LFP of diazirine 1 in isooctane containing 15 mM pyridine

pseudo-first-order decay pathways of the carbene in the absence of pyridine, $k_1 = k_i + k_r[1]$. The quenching reaction of benzylchlorocarbene by 3-chloro-3-benzyl diazirine to form azine has been measured recently⁷ as $k_r = 2 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$. Under LFP conditions ($[1] = 10^{-2} - 10^{-3} \text{ M}$), the contribution from the $k_r[1]$ term is negligible compared with k_i , and hence the intercept can be taken as k_i .

The internal consistency of the kinetics may be checked by the following method. The yield for ylide formation from carbene is given by $\phi_{\text{ylide}} = k_y[\text{py}]/(k_i + k_y[\text{py}])$, where $[\text{py}]$ = pyridine concentration, and the amount of carbene produced in a single pulse is $[\text{carbene}] = \alpha E$, where E is the reading of the energy meter monitoring the laser pulse intensity and α is a proportionality factor. The ylide absorption

is $A = [\text{ylide}] \epsilon l$, and it follows that

$$\frac{1}{A} = \frac{1}{\alpha E} \left(\frac{1}{\epsilon l} + \frac{k_i}{\epsilon l k_y} \times \frac{1}{[\text{py}]} \right)$$

The straight line plot of $1/A$ vs $1/[\text{pyridine}]$ at 25 °C is given in Figure 2, in which the slope and intercept are 0.0675 ± 0.002 and 13.5 ± 1.0 , respectively. Hence the slope/intercept ratio leads to a value of $5.0 \pm 0.4 \times 10^{-3} \text{ M}$ for k_i/k_y , which is in excellent agreement with the $k_i/k_y = 4.4 \pm 0.6 \times 10^{-3} \text{ M}$ obtained by the observed pseudo-first-order rate constants for the increase in the absorption at 380 nm.

In conclusion, the first determination of a 1,2-phenyl migration in a carbene has been reported, $k = 2.0 \times 10^7 \text{ s}^{-1}$ and $\tau = 50 \text{ ns}$. If the A -factor is taken^{1c,1e} to be 10^{11} s^{-1} , then the activation energy for

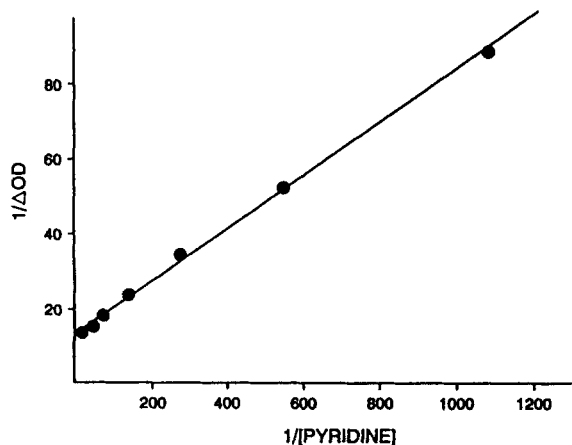


Figure 2. Plot of reciprocal of absorbance versus reciprocal of pyridine concentration at 25 °C

1,2-phenyl migration is *ca* 5 kcal mol⁻¹ (1 kcal = 4.184 kJ). The reaction may be viewed as intramolecular attack by the carbenic vacant p-orbital on the phenyl π -system. The 1,2-H migration in (CH₃)₂CH—C—Cl⁸ is at least five times faster than the corresponding 1,2-phenyl migration in (CH₃)₂CPh—C—Cl and it is twenty times faster than 1,2-methyl migration in (CH₃)₃C—C—Cl.^{1d}

ACKNOWLEDGMENTS

The experiments and analyses of the data produced were performed at the Center for Fast Kinetics

Research, which is supported jointly by the Biomedical Research Technology Program of the Division of Research Resources of the National Institutes of Health (RR00886) and by the University of Texas at Austin. The financial support of NSERC of Canada is gratefully acknowledged.

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