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SHORT COMMUNICATION

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

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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-CH_3 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 aptitude[5] is given as H > Ph > CH_3. 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 method[6] (yield *ca* 5%) and purified by chromatography on silica gel. IR (N=N), 1573 cm^{-1}; UV, λ (MeOH) 340 ($\varepsilon = 63$), 360 ($\varepsilon = 61$); 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 ($CDCl_3$), δ 1·73 (s, 3H), 2·00 (s, 3H) and 7·30 (br s, 5H); ^{13}C NMR ($CDCl_3$), 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, $k_y = 4{\cdot}5 \pm 0{\cdot}2 \times 10^9\ l\,mol^{-1}\,s^{-1}$ and the intercept (extrapolation to [pyridine] = 0) yields the rate constant for the 1,2-phenyl shift, $k_i = 2{\cdot}0 \pm 0{\cdot}2 \times 10^7\ s^{-1}$.

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

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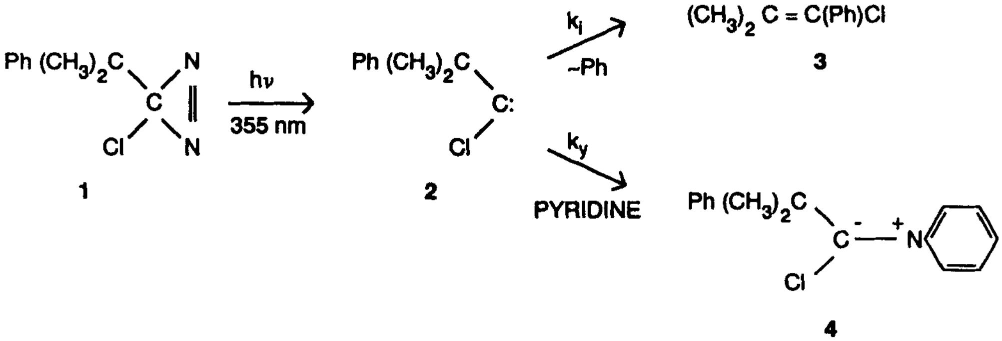

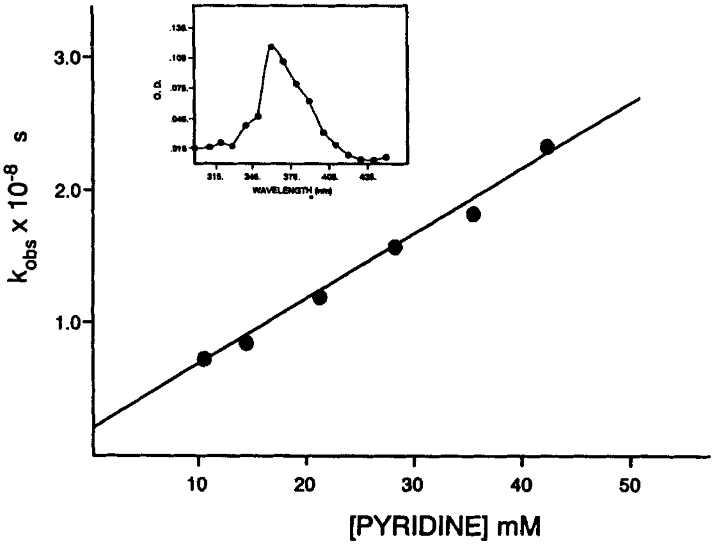

Figure 1. Plot of observed pseudo-first-order rate constants for increase in pyridinium ylide at 380 nm vs pyridine concentration at 25 °C. Inset: transient absorption spectrum of ylide **4** produced by LFP of diazirine **1** in isooctane containing 15 mM pyridine

pseudo-first-order decay pathways of the carbene in the absence of pyridine, $k_1 = k_i + k_r[\mathbf{1}]$. The quenching reaction of benzylchlorocarbene by 3-chloro-3-benzyldiazirine to form azine has been measured recently[7] as $k_r = 2 \times 10^8\ \mathrm{l\,mol^{-1}\,s^{-1}}$. Under LFP conditions ($[\mathbf{1}] = 10^{-2}$–$10^{-3}$ M), the contribution from the $k_r[\mathbf{1}]$ 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 $\phi_{\mathrm{ylide}} = k_y[\mathrm{py}]/(k_i + k_y[\mathrm{py}])$, where [py] = pyridine concentration, and the amount of carbene produced in a single pulse is $[\mathrm{carbene}] = \alpha E$, where E is the reading of the energy meter monitoring the laser pulse intensity and α is a proportionality factor. The ylide absorption is $A = [\mathrm{ylide}]\,\varepsilon l$, and it follows that

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

The straight line plot of $1/A$ vs $1/[\mathrm{pyridine}]$ at 25 °C is given in Figure 2, in which the slope and intercept are $0{\cdot}0675 \pm 0{\cdot}002$ and $13{\cdot}5 \pm 1{\cdot}0$, respectively. Hence the slope/intercept ratio leads to a value of $5{\cdot}0 \pm 0{\cdot}4 \times 10^{-3}$ M for k_i/k_y, which is in excellent agreement with the $k_i/k_y = 4{\cdot}4 \pm 0{\cdot}6 \times 10^{-3}$ 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, $k = 2{\cdot}0 \times 10^7\ \mathrm{s^{-1}}$ and $\tau = 50$ ns. If the A-factor is taken[1c,1e] to be $10^{11}\ \mathrm{s^{-1}}$, then the activation energy for

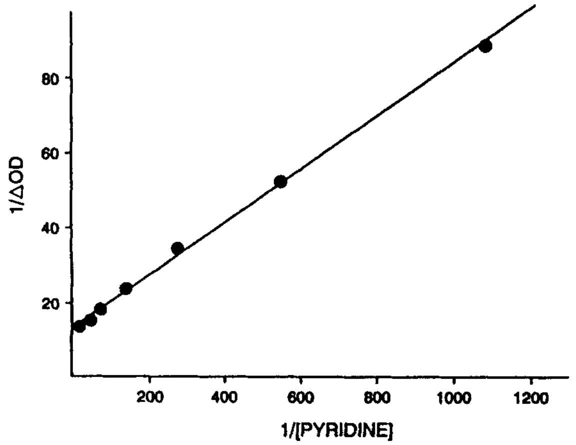

Figure 2. Plot of reciprocal of absorbance versus reciprocal of pyridine concentration at 25 °C

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 $(CH_3)_2CH$—C—Cl[8] is at least five times faster than the corresponding 1,2-phenyl migration in $(CH_3)_2CPh$—C—Cl and it is twenty times faster than 1,2-methyl migration in $(CH_3)_3C$—C—Cl.[1d]

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