# Laser Flash Photolysis Studies: 1,2-Hydrogen Migration to a Carbene

MICHAEL T. H. LIU

University of Prince Edward Island, Charlottetown, Prince Edward Island, Canada C1A 4P3

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The 1,2-H shift is a remarkably ubiquitous and important chemical reaction. It plays a key role in physical organic chemistry. The 1,2-migration of a hydrogen to the carbene center generating an alkene[1-5] is the most common rearrangement of singlet carbenes. This is generally viewed as a facile process. The rearrangement takes place when the migrating group carries its electrons into the vacant orbital of the singlet state. Hoffmann et al.,[6] in a semiempirical MO theory presented in 1968, predicted that the hydrogen which migrates to the electron deficient carbon would align with the empty orbital (LUMO).
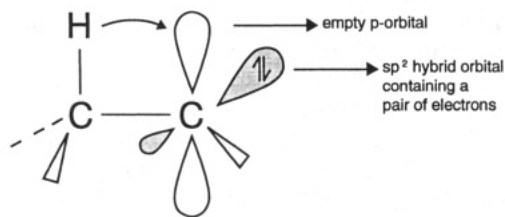
The simplicity of the 1,2-hydrogen migration has attracted numerous theoretical investigations. Early calculations[4,7-13] deduced energy barriers to this rearrangement ranging from 0 to 27 kcal mol^{-1}. The original 0 value,[7,8] obtained by the semiempirical MINDO method, was considered unreliable because of the known deficiency of MINDO in favoring cyclic structures. Ab initio methods gave large values,[10,11] but more sophisticated calculations, involving polarized functions and correlation effects, reduced the value of the energy barrier to 2.1 kcal/mol.[12] Recently, Evanseck and Houk[14] carried out theoretical calculations on the activation energies for 1,2-H shifts in singlet carbenes by using MP4/6-311G** energies calculated on MP2/6H31G*-optimized geometries. The predicted activation energies for methylchlorocarbene, cis- and trans-methylhydroxycarbene, cis- and trans-methylmethoxycarbene, trans-methylvinylcarbene, and allylmethylene are 11.5, 24.9, 24.5, 23.1, 26.9, 8.4, and 0.0 kcal mol^{-1}.

Experimental work on 1-aryl-2-diazopropanes has produced evidence for the existence of a barrier to a 1,2-H shift in dialkylcarbenes, even though no absolute value could be assigned.[15] The effect of temperature on the E/Z product ratio in the photolysis of

Michael T. H. Liu, Professor of Chemistry at the University of Prince Edward Island, obtained his B.Sc. degree from St. Dunstan's University, Charlottetown, Prince Edward Island, in 1961. Upon graduation with his M.A. in chemistry from St. Francis Xavier University in 1964, he was group leader in R & D at Chemcell Ltd., Quebec, but later returned to his studies with K. J. Laidler and was awarded his Ph.D. in 1967 from the University of Ottawa. In the same year he received a National Research Council Overseas postdoctoral fellowship tenable at the University of Reading under the direction of H. M. Frey. He joined the Chemistry Department at the University of Prince Edward Island the following year. Dr. Liu's current research interests include the kinetics of the 1,2-hydrogen migration in carbenes and ylides and organic synthesis involving carbenes.

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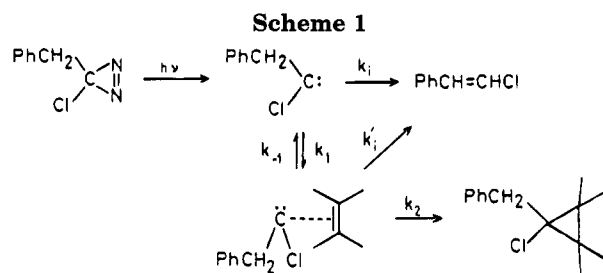PhCN$_2$CHMePh and PhCN$_2$CH$_2$R also points to the existence of a finite barrier for 1,2-H shifts in aralkylcarbenes.[16] Lineberger and co-workers[17] had examined the vibrational structure of the vinylidene photoelectron spectrum and suggested the presence of a significant barrier to the formation of acetylene. Recently, the products derived from the thermolysis of 4-diazirinopentanoic acid yielded an estimate of 1.1 ± 1 kcal/mol for the height of the barrier[18] for 1,2-H shifts in dialkylcarbenes.

Intramolecular reactions generally are faster than intermolecular reactions, and so they predominate in the reaction of singlet carbenes. Although many trapping experiments have been performed, the absolute rate constants for 1,2-H migration in singlet carbenes were not determined until the late 1980s. Within the past several years numerous specific rate constants and activation energies have been reported for 1,2-H migration in carbenes.

Relative Rate Studies

In 1984, the kinetic studies of Tomioka et al,[19] on the photolysis of 3-chloro-3-benzyldiazirines in the presence of alkenes provided evidence for the intervention of a carbene–alkene complex. Irradiation of aryl-substituted 3-chloro-3-benzyldiazirines in cyclohexane with (Z)-4-methyl-2-pentene gave (Z)- and (E)-β-chlorostyrenes and cyclopropanes. The plot of the intermolecular/intramolecular product ratio as a function of alkene concentration showed a pronounced curvature. The "simple competition" is inconsistent with these results because it predicts that the product ratio would be linear with respect to alkene concentration. However, the intervention of a reversibly formed intermediate of carbene with alkene readily accounts for the curvature of the plot.

Liu and co-workers[20,30] extended these experiments by examining the decomposition of 3-chloro-3-benzy-

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Scheme 1

lidiazirine in the presence of tetramethylethylene (TME). The decomposition in the presence of TME affords a measure of cyclopropanation in competition with intramolecular hydrogen transfer to yield (Z)- and (E)-β-chlorostyrenes. The chlorostyrenes are proposed to be formed by two pathways: one from the free carbene, the other from decomposition of the complex, because the Z/E ratio of chlorostyrene increased as the concentration of TME increased. In addition, plots of intermolecular/intramolecular product ratios vs [TME] are nonlinear in thermolysis as well as in photolysis.

The application of a steady-state treatment of Scheme 1 leads to the following expression:

$$\frac{chlorostyrene}{cyclopropane} = \frac{k_i'}{k_2} + \frac{k_i}{k_t}\frac{1}{[TME]} \qquad (1)$$

where the overall trapping rate constant, k_t, equals

$$k_1 k_2/(k_{-1} + k_2 + k_i')$$

Temperature studies on product ratio as a function of [TME] allow the determination of $E_i - E_t$, where E_i is the activation energy for the 1,2-H shift in benzylchlorocarbene and E_t is the activation energy for cyclopropanation. Assuming that $E_t = -1.7$ kcal mol^{-1} because of the similarity between C$_6$H$_5$ĊCl[21] and C$_6$H$_5$CH$_2$ĊCl, the activation energy, E_i, for the 1,2-H shift was calculated to be 6.4 kcal mol^{-1}. As far as we know, this is the first experimental report of an energy barrier for the 1,2-shift. Although the estimate is ±2 kcal mol^{-1}, this activation energy provides a valuable beginning for the evaluation of factors that control this intramolecular rearrangement. Similarly, the activation energy for 1,2-hydrogen migration in benzylbromocarbene[22] was estimated to be 4.7 kcal mol^{-1}.
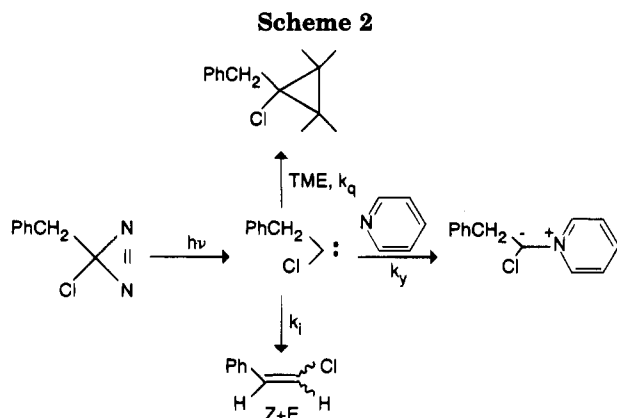
Benzylchlorocarbene generated in a nonpolar solvent, such as cyclohexane, is readily trapped by alkene. In a polar solvent, such as acetonitrile, the intermolecular process competes poorly with the intramolecular 1,2-H shift, because the singlet carbene may already be solvated, or possibly, it may have formed an ylide. In either case, it would be less susceptible to attack by external alkene.[23]

Laser Flash Photolysis: Pyridine Ylide Probe Technique

The availability of powerful commercial lasers, transient digitizers, and other electronic components offers the organic photochemist attractive opportunities to engage in laser flash experiments to understand carbene reactivity.

Alkylchlorocarbenes and species that lack a chromophore are believed to be invisible to laser experiment with UV–vis detection. Inspired by Scaiano's

Scheme 2

kinetic probe technique,[24] Jackson et al.[25] applied the pyridine probe to the studies of phenylchlorocarbene and *tert*-butylchlorocarbene. This permitted measurement of the first absolute rate constant of an "invisible" alkylchlorocarbene, which lacks a suitable chromophore for being detected directly. Many studies on the lifetimes of alkylhalocarbene followed this discovery, including the rates of 1,2-hydrogen migration in $CH_3\ddot{C}Cl$ (330 ns),[26] $C_2H_5\ddot{C}Cl$ (10 ns),[27] $C_3H_7\ddot{C}Cl$ (10 ns),[27] i-$C_3H_7\ddot{C}Cl$ (10 ns),[27] $C_6H_5CH_2\ddot{C}Cl$ (~18 ns),[28] and $C_6H_5CH(CH_3)\ddot{C}Cl$ (1 ns).[27]

Laser flash photolysis of 3-chloro-3-benzyldiazirine[29] in isooctane produces benzylchlorocarbene, which reacts with pyridine to form an ylide ($\lambda = 380$ nm) or undergoes 1,2-hydrogen migration to form (*Z*)- and (*E*)-β-chlorostyrenes, Scheme 2. The rate constant for the 1,2-H migration, k_i, is determined by plotting the pseudo-first-order rate constants, k_{obsd}, for the growth of the ylide vs [pyridine] and extrapolating to [pyridine] = 0. Hence, $k_{obsd} = k_i + k_y$[pyridine] and k_y is the rate constant for the reaction of the carbene with pyridine. At 25 °C, $k_i = 6 \times 10^7$ s^{-1} ($\tau = 17$ ns), and k_y (8×10^9 M^{-1} s^{-1}) is close to diffusion controlled, which characterizes reaction of chlorocarbene with pyridine. From such measurements, performed at various temperatures, the kinetic parameters $E_i = 4.5$ kcal mol^{-1} and $A_i = 10^{11.1}$ s^{-1} were obtained.

Support for the assignment of the ylide at 380 nm stems from the observation that the rate of ylide formation is first-order in pyridine concentration and that the addition of olefin quencher, such as tetramethylethylene, increases the apparent rate constant for ylide formation and decreases the yield of the ylide because the cycloaddition of the carbene to the olefin competes with ylide formation.

$$k_{obsd} = k_i + k_y[\text{pyridine}] + k_q[\text{TME}]$$

The quenching rate constant, k_q, for the reaction of benzylchlorocarbene with TME has been determined as 6×10^8 M^{-1} s^{-1}. The absorption spectrum of benzylchlorocarbene is shown in Figure 1. The temperature dependence of k_i was determined by direct observation, at 310 nm, of the decay of the carbene. The kinetic parameters, $E_i = 4.83$ kcal mol^{-1} and $A_i = 10^{11.3}$, resemble those derived from the pyridine technique.

Substituent Effects

Relative-rate studies on substituted 3-chloro-3-benzylidiazirines in alkenes that yield cyclopropanes and

chlorostyrenes have been reported.[30] These results suggest that the cyclopropanation of benzylchlorocarbenes is independent of substituents on the phenyl ring. This conclusion has now been substantiated[31] by the absolute rate constants for cycloaddition of benzylchlorocarbene, p-$CF_3C_6H_4CH_2\ddot{C}Cl$, and p-ClC_6H_4-$CH_2\ddot{C}Cl$ to TME, for which the k_q values are 6.2×10^8, 5.7×10^8, and 5.5×10^8 M^{-1} s^{-1}, respectively. In particular, the cyclopropanation of p-$ClC_6H_4CH_2\ddot{C}Cl$ with TME gave a negative activation energy of -4.7 kcal mol^{-1}. A negative activation energy for cyclopropanation may be explained in terms of a carbene–alkene complex.[30] The complex model is particularly useful because it provides a way to rationalize the variations of the *Z/E* ratio of chlorostyrenes vs TME concentration. However, Houk and Rondan,[32] using high-level calculation, have advanced the alternative interpretation that negative activation energies can arise in fast reactions because $\Delta S^{\ddagger}$ is large and negative, so that the temperature dependence of the free energy barrier is entropy-controlled. The Houk model accounts well for the negative activation energy and has been discussed in detail in a recent review.[33]

A combination of laser flash photolysis[31] and relative rate studies[30] found that the 1,2-hydrogen migration is accelerated by OCH_3 or CH_3 substituents and is decelerated by Cl or CF_3 substituents on the phenyl ring of $XC_6H_4CH_2\ddot{C}Cl$. A Hammett plot of the logarithms of the rate constants for 1,2-H migration vs the σ_p value gave a ϱ value of -1.0, consistent with a hydride-like 1,2-H shift to the carbene center.
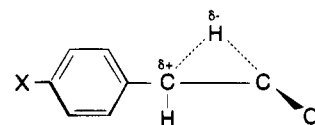
Mechanisms of Carbene Formation

In 1989, LaVilla and Goodman,[34] using time-resolved photoacoustic calorimetry, reported the absolute rate constants and the thermal chemistry for the 1,2-hydrogen shift in alkylchlorocarbenes. The Arrhenius parameters for $CH_3\ddot{C}Cl$ yielded $E_a = 4.9$ kcal mol^{-1} and $\log A = 9.7$. The calculated activation energies for the rearrangement of $CH_3CH_2\ddot{C}Cl$ and $(CH_3)_2CH\ddot{C}Cl$ are ≤ 2.4 kcal mol^{-1}. The combination of photoacoustic calorimetry and product studies on the photochemical decomposition of methylhalodiazirines allowed LaVilla and Goodman[35] to propose a two-pathway mechanism for the formation of vinyl halides.

When CH_3OH or TME was used as a carbene quencher, the partition quantum yields in both substrates were identical. These results point to the fact that the ratio of inter- to intramolecular carbene products depends on both the relative rate constants k_i vs k_2 and the relative rate constants for carbene and

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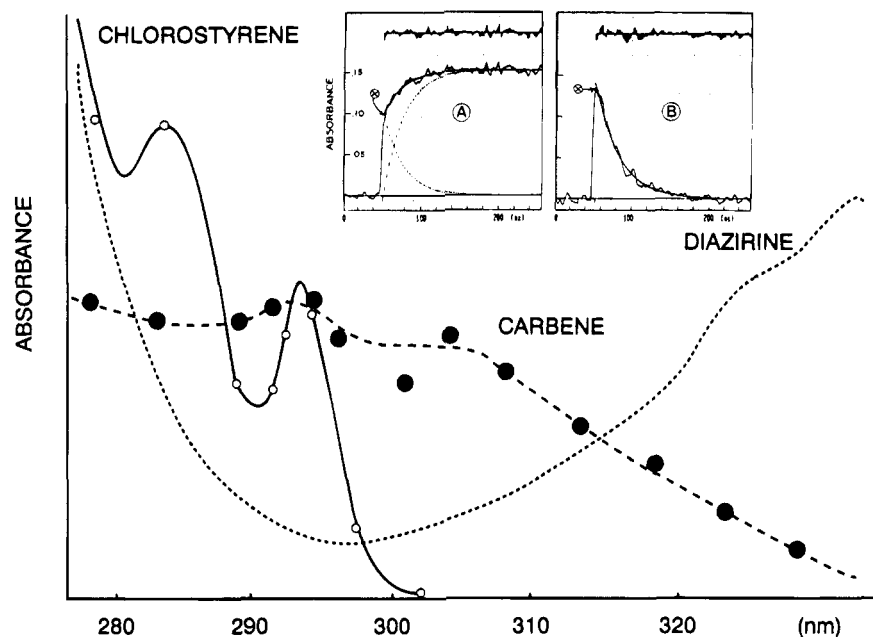
Figure 1. Absorption spectra of β-chlorostyrenes (solid line) and benzylchlorodiazirine in isooctane (dotted line) recorded on a conventional spectrophotometer, and transient absorptions measured in LFP 4 ns (●) and 100 ns (○) after the excitation. Inset: Transient absorbance signal obtained at 280 nm (A) and 310 nm (B) by LFP of diazirine in isooctane at ≈ 15 °C: The 280-nm trace may be analyzed as the sum of the absorptions of the carbene and of the β-chlorostyrene, respectively. The 310-nm trace can be fitted with a single exponential decay.

Scheme 3
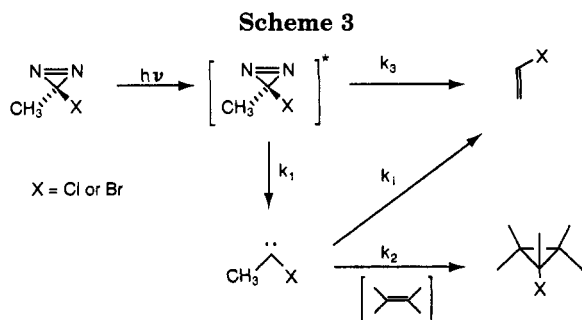
vinyl halide formation, k_1 vs k_3. The absence of intermolecular carbene trapping products may result from the inefficient photochemical formation of carbenes from alkylhalodiazirine precursors ($k_3 \gg k_1$) and is not due to the prohibitively rapid rate of their rearrangement ($k_i \gg k_2$).

The kinetic studies obtained thus far for alkylchlorodiazirines may be interpreted in terms of *two* pathways for the formation of chloroalkenes. The first is the 1,2 intramolecular hydrogen shift of the initially formed carbene. An additional pathway involving the carbene—alkene complex,[30] excited carbene,[36] diazo compound,[37] or excited diazirine[35,38,39] has been proposed. According to Scheme 3,

$$\frac{\text{vinylhalide}}{\text{cyclopropane}} = \frac{k_3}{k_1} + \frac{k_i(k_1 + k_3)}{k_1 k_2}\frac{1}{[\text{TME}]} \quad (2)$$

Comparing eqs 1 and 2, a plot of the ratio of the rearranged and addition product *vs* 1/[TME] yielded a straight line with slope equal to k_i/k_t for the complex model[30] or $k_i(k_1 + k_3)/(k_1 k_2)$ for the excited state

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model.[35] The overall trapping rate constant, k_t, is in fact equal to k_2 only if the concurrent 1,2-H shift in the excited diazirine is unimportant, i.e., if $k_1 \gg k_3$. Since the rate constants for 1,2-H shifts in benzylchlorocarbene (k_i) and its addition to TME (k_2) have been determined by laser flash photolysis,[29] a value of ~ 0.10 was obtained for k_i/k_2 at 25 °C, in excellent agreement with the value (slope = 0.10 at 25 °C) obtained[20] from the linear plot of eq 1 or 2. Had the equation $k_i(k_1 + k_3)/(k_1 k_2)$ not been reduced to k_i/k_2, the Arrhenius law would not have applied. The collinearity[30] of the Arrhenius plots suggests that the concurrent 1,2-H shift in the excited diazirine is *not* important and confirms the importance of the carbene—alkene complex in the photolysis of benzylchlorodiazirine. In agreement with this absence of excited diazirine, White and Platz[37] have also reported that fluorescence was not observed in benzylchlorodiazirine either at room temperature or in glassy 3-methylpentane at −196 °C.

Upon LFP of alkylchlorodiazirine, White and Platz[37] have shown that the optical yield of the pyridinium ylide at saturation ([pyridine] ~ 0.5 M) mirrors the relative yield of ylide, assuming that the extinction coefficients of the ylides are independent of the nature of the alkyl group. It is reasonable to assume that the optical yield of the ylide at saturation tracks the yield of carbene produced in the laser pulse for a given diazirine. They have demonstrated that the yield of carbene at saturation correlates closely with the bond dissociation energy of the C—H bond α to the ring carbon. Therefore, the variation in the yield of ylide reflects the efficiency with which the excited diazirine is converted to carbene. Conversely, the correlation between the yield of pyridine ylides and the strength of the migrating C—H bond might reflect the ease of 1,2-H migration in the ylide to yield the rearrangement product and the release of pyridine. This proposal may mirror the lifetime of the free carbene

Scheme 4
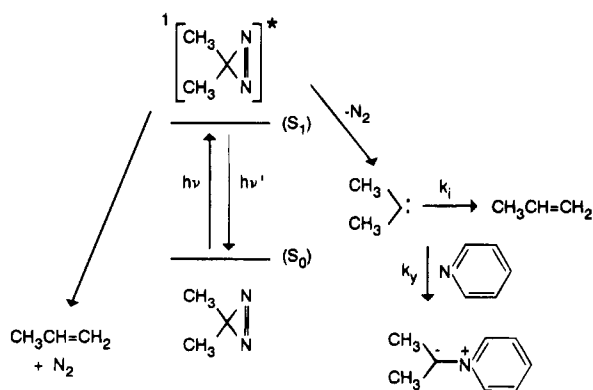
with $(CH_3)_2CHCCl$ (<10 ns), CH_3CCl (300 ns), and c-C_3H_5CCl (~2 μs).

Excited Diazirine Chemistry

Platz and co-workers[38,39] have presented the most convincing data for excited state chemistry of diazirine photolysis. Pulsed laser excitation of 3,3-dimethyl-diazirine (DMD) in pentane produces a highly structured fluorescence spectrum, with a mirror-image relationship between the emission and the fluorescence excitation spectra. The fluorescence of 3,3-dimethyldiazirine-d_6 (DMD-d_6) is 1.5 times more intense than that of DMD. The fluorescence of DMD or DMD-d_6 is not quenched by pyridine, suggesting that the diazirine excited state does not react with pyridine. The fluorescence intensities of the diazirines increase with decreasing temperature. The loss in fluorescence intensity is associated with activation energies of 1.5 and 1.0 kcal mol^{-1} for DMD-d_6 and DMD, respectively. The amount of pyridinium ylide obtained at a high concentration of pyridine is significantly larger for DMD-d_6. This result implies that the deuteration reduces the 1,2-H migration concurrent with nitrogen extrusion in the diazirine excited state. Thus, the yield of dimethylcarbene-d_6 produced from DMD-d_6 is larger than the corresponding dimethyl-carbene-d_0 from DMD.

Generally, photolysis of DMD is consistent with a mechanism in which an electronically excited singlet state is produced which decays by three competitive pathways: (a) fluorescence, (b) carbene formation, and (c) α-hydrogen migration concurrent with nitrogen extrusion, Scheme 4.

Frey and Stevens first proposed the direct photochemical formation of an alkene from the excited state of a diazirine in 1965.[40] They postulated that the photolysis of diazirines produces the carbene in an excited singlet state; whereas, thermolysis produces a carbene in its lowest singlet state. Many subsequent reports[3a,41,42] shared a similar view to account for the products formed by thermolysis and photolysis of diazirine or other carbene precursors. These results suggest that a single intermediate cannot be reponsible for the formation of products in thermolysis as well as in photolysis.

In 1985, Müller-Remmers and Jug[43] published important MO calculations for the excited states of DMD. Their semiempirical method, including configuration interaction, is superior to MINDO/3 and MNDO. They found that the HOMO of DMD is n$_-$ (nonbonding) and the LUMO is π^*. Excitation at 350 nm promotes the electron from S_0 to $S_1(n\pi^*)$, which is fluorescent. However, there is an upper state $S_2(n\sigma^*)$ which extrudes nitrogen. Because of the barrier for excited state surface crossing, the intensity of fluorescence from S_1 is stronger at lower temperatures, in agreement with the results obtained by Platz.[38,39,44] Platz and co-workers[45] used the pyridine probe technique to study the lifetimes of a series of alkylaryl-carbenes in pentane solution at 25 °C. LFP (308 nm) of diazo precursors in the presence of pyridine produced the transient spectra of the ylides (λ = 420$-$450 nm). The lifetimes of the carbenes were determined by the double-reciprocal method. The ratio of slope to intercept yields $k_{1,2}/k_yK$, where K is the equilibrium constant of the singlet and triplet carbene. Assuming that k_yK had a value of 2×10^7 M^{-1} s^{-1}, the lifetimes of the carbenes could be calculated. Thus, the values are PhCCH$_3$ (595$-$833 ns), PhCCD$_3$ (535$-$885 ns), PhCCH$_2$CH$_3$ (119 ns), PhCCH$_2$CH$_2$CH$_3$ (114 ns), c-C_3H_5CPh (128 ns), c-C_4H_7CPh (134 ns), c-C_5H_9CPh (241 ns), and c-$C_6H_{11}CPh$ (320 ns).

The relative intensity of the pyridine ylide formation from alkyl aryl diazo compound tracks the percent yield of the carbene. These data demonstrate that the excited states of the diazo compound also suffer hydrogen migration with direct alkene formation in a manner reminiscent of diazirine photochemistry. Among all the diazo compounds studied, the isopropyl phenyl diazomethane gave a very low intensity of the ylide absorption. Hence the lifetime of the carbene, i-C_3H_7CPh, could not be determined accurately. It is believed that the excited state of isopropylphenyldiazomethane largely experienced 1,2-hydrogen migration.

The rearrangement of methylcarbene to ethylene represents one of the simplest 1,2-H shifts in an alkyl-substituted carbene. Evanseck and Houk[14] theoretically predicted an activation barrier of 0.6 kcal mol^{-1} for this reaction. Methylcarbene has a triplet ground state, but the lowest excited singlet state is only 3$-$5 kcal mol^{-1} higher in energy, as indicated by the recent *ab initio* studies of Schaefer[46] and of Carter.[47] The key question here is whether singlet methylcarbene is a transition state or an intermediate. Seburg and McMahon[48] showed recently that methylcarbene can be trapped at 10 K in a carbon monoxide matrix to yield the ketene product. It is also possible to intercept methylcarbene with alkene or phenylsilane, albeit in low yield.[49] LFP of methyldiazirine in the presence

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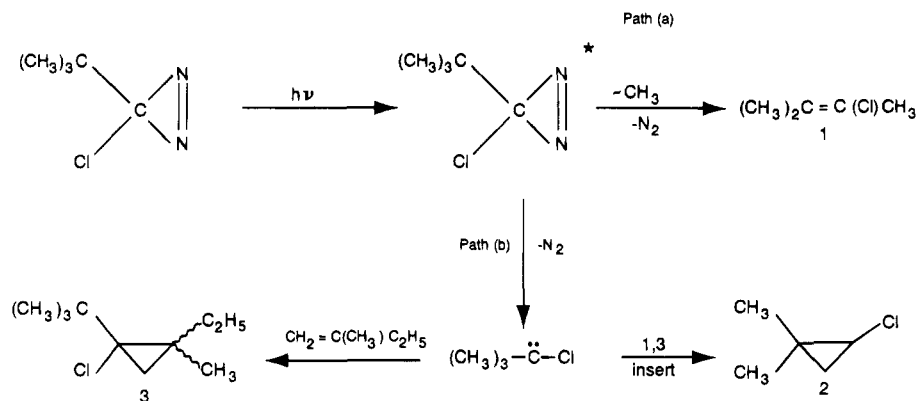
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Scheme 5

of pyridine/pentane fails to generate the ylide absorption even at as low a temperature as −40 °C. However, LFP of methyldiazirine-d_4 in pyridine/pentane produces the transient absorption spectrum of the ylide.[50] A double-reciprocal plot of the optical yield of the ylide *vs* pyridine concentration allows the determination that the lifetime of methylcarbene-d_4 is 500 ps in pentane. The activation energy for 1,2-deuterium shift in $CD_3\ddot{C}D$ is calculated to be 2−3 kcal mol^{-1}. This agrees with the calculations of Evanseck and Houk[14] and the recent theoretical prediction of Ma and Schaefer.[51]

1,2-C, 1,2-CH₃, 1,2-Cl and 1,2-C₆H₅ Migrations

LFP of 3-chloro-3-cyclopropyldiazirine in isooctane[52] yields a transient absorption attributed to cyclopropylchlorocarbene (λ = 250 nm). The Arrhenius parameters for the 1,2-C migration are $\log A = 11.1$ and $E_a = 7.4$ kcal mol^{-1}. Moss and co-workers[53] reported on the matrix spectroscopy and the LFP of 3-chloro-3-cyclopropyldiazirine. The diazirine was isolated in a nitrogen matrix at 12 K and irradiated at 335 nm, affording the carbene, which showed strong IR absorptions. LFP of the diazirine produced the transient absorption at 255 nm. The decay of the cyclopropyl-chlorocarbene at 20 °C obeyed good first-order kinetics over 90% of the reaction; $k_{1,2} = 9 \times 10^5$ s^{-1}. Arrhenius analysis gave $E_a = 3.8$ kcal mol^{-1} and $\log A = 8.74$. These results differ from those reported by Liu and Bonneau.[52] In the latter work, the carbene decay at 20 °C was always composed of a mixture of first- and second-order processes. The first-order rate constant can be extracted after correcting for the dimerization process. According to Moss,[53] the difference between the results lies in the relative roles of enthalpy and entropy. In any event, both laboratories arrived at similar $\Delta G^{\ddagger}$ values (9−10 kcal mol^{-1}) for the 1,2-C migration.

Moss and co-workers[54] examined the 1,2-C migration of cyclopropylmethoxycarbene and found that the carbene readily undergoes reaction with alkene and methanol. However, the intramolecular 1,2-C migration is suppressed ($k < 3 \times 10^3$ s^{-1}) by the presence of the methoxy substituent, in agreement with the prediction of Evanseck and Houk.[14] Moss and co-workers have further demonstrated the effect of a fluorine substituent on 1,2-H and 1,2-C migrations in a series of alkylfluorocarbenes *vs* alkylchlorocarbenes: $C_6H_5OCH_2\ddot{C}X(\sim H)$; $(CH_3)_3C\ddot{C}H_2\ddot{C}X(\sim H)$; c-$C_4H_7\ddot{C}X(\sim H$ and $\sim C)$; c-$C_3H_5\ddot{C}X(\sim C)$ and X = F or

Cl. In keeping with the theoretical calculations,[14] each of the five Cl/F comparisons, the rate constants for 1,2-H or 1,2-C shifts are greater for $R\ddot{C}Cl$ than $R\ddot{C}F$. However, the differences in $R\ddot{C}Cl/R\ddot{C}F$ rate constants and activation energies are not as great as predicted by theory.[14] Conceivably, tunneling may play a role, especially in 1,2-H migration.

Although there appears to be little contribution to product formation from excited cyclopropylchlorodiazirine,[52,53] photolysis of 3-(2,3-dimethylcyclopropyl)-3-chlorodiazirine[55] in the presence of trimethylethylene points to the fact that electronically excited diazirine was involved in product formation. In the LFP of cyclobutylchlorodiazirine, Moss and Ho[56] reported the kinetics of the intramolecular reactions of chlorocyclobutylcarbene, affording chlorocyclopentene and chloromethylenecyclobutane. These authors also investigated the effect of external alkene on the distribution of rearranged and additional products. They concluded that the excited state of the diazirine suffers both carbon and hydrogen migration in addition to carbene formation.

The most innovative and convincing evidence for excited diazirine comes from the recent photolysis of 3-*tert*-butyl-3-chlorodiazirine[57] yielding 2,2-dimethyl-1-chlorocyclopropane (2) and 2-chloro-3-methyl-2-butene (1) as products. Photolysis of the diazirine in 2-methyl-1-butene afforded cyclopropane adduct 3 in addition to the products 1 and 2, see Scheme 5. When the product distribution of this reaction was studied as a function of [2-methyl-1-butene], the ratio of intermolecular/intramolecular product, 3/2, was linear with alkene concentration. The yield of 1,2-CH₃ shift product, 1, was independent of the alkene concentration; this suggests that 1 was formed exclusively from the excited diazirine. These results clearly demonstrate that the carbene partitioned directly into products 2 and 3; the role of carbene−alkene complexes in these reactions therefore must be insignificant.

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Moss and Ho[58] recognized that the lifetime of $(CH_3)_3CCCl$ is controlled by the reaction of the carbene with the diazirine which enables them to form azine. When extrapolating the values of k_{obsd} to [pyridine] = 0, the lifetime of the carbene was longer than 1 μs. In this connection, Liu and Chateauneuf[59] used the combination of LFP and product analysis to demonstrate that even though $C_6H_5OCH_2CCl$ reacted with diazirine precursor, with a substantial rate constant of 3.5×10^8 M^{-1} s^{-1}, the predicted azine product was not formed. These results indicate that either carbene/diazirine reversibility or subsequent hydrogen migration of the carbene/diazirine adduct.

Cyclopropylcarbene is of special interest because of its simple ring expansion which enables it to yield cyclobutene. LFP of cyclopropyldiazirine[60] in pentane fails to yield a detectable transient absorption. However, LFP of the diazirine in the presence of pyridine at 25 °C produces the ylide absorption at $\lambda = 379$ nm. A double-reciprocal plot of 1/OD vs 1/[pyridine] produces a lifetime of 24 ns in pentane. LFP of dicyclopropyldiazirine in pentane yields a transient absorption attributed to dicyclopropylcarbene ($\lambda = 235$ nm, $\tau = 32$ ns). The lifetimes determined by direct detection are in good agreement with those using the pyridine method.

Few investigations involving 1,2-chlorine migration to a carbene center have been reported. LFP of 3-(α,α-dichlorobenzyl)-3-chlorodiazirine[61] containing pyridine produces an ylide absorption at $\lambda = 370$ nm. The straight line plot 1/OD vs 1/[pyridine] leads to the determination of the lifetime for $C_6H_5CCl_2CCl$ ($\tau = 33$ ns). Photolysis of 3-(α-methyl-α-chlorobenzyl)-3-chlorodiazirine[62] in isooctane results in the formation of α-methyl-β,β-dichlorostyrene. In the presence of tetramethylethylene, the cycloadduct is also formed in competition with the intramolecular 1,2-chlorine shift to the carbene, $C_6H_5C(Cl)CH_3CCl$. Relative rate studies have estimated the lifetime of the carbene to be ~1 ns and, therefore, beyond direct spectroscopic detection in the nanosecond regime.

As predicted, LFP at 355 nm of 3-(α-methyl-α-chlorobenzyl)-3-chlorodiazirine[63] in isooctane at 21 °C resulted in a transient absorption signal observed within the excitation pulse that closely followed the time profile of the laser pulse. The absorption signal ranged from 290 to 340 nm, similar to that of parent benzylchlorocarbene. When monitored at 310 nm, the first-order rate constants for decay of the carbene were measured from −20 to −71 °C, which resulted in the Arrhenius parameters $E_a = 3.40$ kcal mol^{-1} and log A (s^{-1}) = 10.98.

LFP or 3-(α,α-dimethylbenzyl)-3-chlorodiazirine[64] led to the first determination of a rate constant for a 1,2-phenyl shift in $C_6H_5C(CH_3)_2CCl$ ($\tau = 50$ ns). This confirmed the migratory aptitude as H > C_6H_5 > CH_3.

Kinetic Isotope Effect

In the LFP of dimethyldiazirine, Platz and co-workers[38] noticed a significant isotope effect on the lifetime of dimethylcarbene in pentane at ambient temperature, $\tau_D/\tau_H = 3.2$. These authors concluded that the large isotope effect may be due to a contribution of quantum mechanical tunneling to the hydrogen migration reaction. Moss and co-workers[65] have also reported a large kinetic isotope effect of $ca.$ 5 for the 1,2-H/1,2-D shift in neopentylfluorocarbene. Goodman and co-workers[66] had examined the 1,2-H migration of methylchlorocarbene over the 248−343 K temperature range. They found that the Arrhenius plot of ln k_H vs 1/T is curved and that k_H/k_D increases commensurately with a rise in temperature. In accordance with the calculations by Storer and Houk,[67] Goodman[66] proposed the application of quantum mechanical tunneling for 1,2-H(D) shifts in methylchlorocarbene. According to these authors, the formation of vinyl chloride could arise from two pathways. One might occur by movement over the classical barrier, while the other might result from quantum mechanical tunneling. The curved Arrhenius plot could be the result of two competing pathways having different activation energies. The isotope effect could increase with the temperature if the two pathways had different isotope effects. As with Goodman's results, LFP of 3-chloro-3-benzyldiazirine and 3-chloro-3-(phenyldideuteriomethyl)diazirine in isooctane over the 60 to −80 °C temperature range also resulted in curved Arrhenius plots for both 1,2-H and 1,2-D migration in benzylchlorocarbene.[68] The k_H/k_D values increased smoothly from 0.87 to 2.62 when the temperature increased from −60 to 30 °C. The k_H/k_D value was approximately 4 for most of the temperatures studied if a solvent correction was applied. Quantum mechanical tunneling or the influence of the solvent may be a possible explanation for observations over these temperature ranges. However, Wierlacher et al.[69] recently reported that, in the photolysis of 3-chloro-3-benzyldiazirine and 3-chloro-3-(phenyldideuteriomethyl)diazirine in cryogenic matrices, quantum mechanical tunneling (QMT) played a significant role at very low temperatures (30 K). It is also conceivable that QMT may be important in solution chemistry.

Conclusion

It is appropriate to ask the same question that was raised by Schaefer[4] some 15 years ago, "What have we learned concerning the 1,2-H shift from these laboratory studies?" The obvious answer is that many of the rate constants and activation parameters for 1,2-H migration in a variety of carbenes are now known. The use of laser flash photolysis permits the characterization of many transient species and allows the further understanding of mechanistic pathways. The involvement of excited diazirine is evident in

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several studies, especially in the photolysis of dimethyldiazirine. However, we must be cautious since this may not be a general phenomenon for all diazirine photolyses. According to Jug,[43] the excited diazirine molecule in the S_1 state ($n\pi^*$) must overcome a small energy barrier to reach the S_2 state ($n\sigma^*$), which is dissociative and correlates directly with the $^1C:^* + N_2$. Thus, the carbene should be produced in its excited state, but at some point, the surface connecting the S_2 state to $^1C:^* + N_2$ is close to the surface connecting the diazirine ground state to $^1C: + N_2$. Hence, a radiationless transition may produce *some* ground state carbene from the excited state surface. The percentage of ground state carbene should therefore be determined by the efficiency of this process and could be very sensitive to any modification of the molecular structure of the diazirine, such as isotopic substitution. Further studies, both theoretical and experimental, will shed light on this complicated, yet interesting, topic.