0.65 g (0.94 mM) of precyclophane **6b** in 43 mL of pyridine. After standing overnight, the solvent was separated by distillation in vacuo. The residue obtained was taken up in CH_2Cl_2 and washed with water. The organic concentrate was chromatographed on silica gel with CH_2Cl_2 as eluent to give 79 mg of a pale yellow solid. Crystallization from CH_2Cl_2 afforded 41 mg (6% yield) of cyclophane **1b**: mp >250 °C; *m/e* 687.1893 (Calcd for $C_{43}H_{29}NO_8$, 687.1893); δ ($CDCl_3$) 8.11 (2 H, s, H_1), 7.86 (1 H, tr, J = 8 Hz, py-H_4), 7.71 (2 H, d, J = 8 Hz, py-$H_{3,5}$), 7.47 (2 H, d, J = 9 Hz, H_5), 7.19 (2 H, s, H_4), 7.04 (2 H, dd, 9, 2.4 Hz, H_6), 7.01 (2 H, s, H_8), 6.85 (4 H, s, xylyl), 5.5 (4 H, AB q, J = 11 Hz, py-CH_2), 5.31 (4 H, s, CH_2-xylyl), 4.84 (4 H, s, $CH_2C{\equiv}C$).

Determination of Association Constants. (A) Titration Method. The cyclophane (1–2 mg in 0.5 mL of deuterated solvent) was titrated with appropriate amounts of a stock solution of *p*-nitrophenol in the same solvent. By integration of the NMR spectrum, the number of equivalents of phenol was determined. At the conclusion of the experiment, a known quantity of dichloroethane was added to determine the host concentration. A best fit for the plot of chemical shift of the H_1 naphthalene proton versus the guest–host concentrations was obtained with a nonlinear least-squares method.

(B) Competition Method. The two cyclophanes to be compared (1–2 mg each) were dissolved in 0.5 mL of CD_2Cl_2 and varying amounts of *p*-nitrophenol were added. From comparison of the observed upfield chemical shift ($\delta_0 - \delta_{obsd}$) of the naphthalene H_1 proton to that of the chemical shift of the complex ($\delta_0 - \delta_{complex}$), F_1 and F_2 were obtained, and K_{rel} was calculated (eq 1). The chemical shift of H_1 in the complexes was assumed to be that which is observed when the guest–host ratio is large.

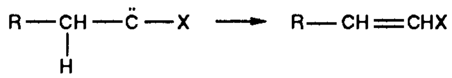
Benzylchlorocarbene: Kinetics Parameters for 1,2-H Migration, UV Absorption Spectrum, and Mechanism for Addition to Alkenes[†]

Michael T. H. Liu[*,‡] **and Roland Bonneau**

Contribution from the UA 348 du CNRS, Laboratoire de Chimie Physique A, Université de Bordeaux I, 33405 Talence, France. *Received June 6, 1989*

Abstract: Laser flash photolysis (LFP) of 3-benzyl-3-chlorodiazirine, **1**, in isooctane, produces benzylchlorocarbene which reacts with pyridine to form an ylide or undergoes 1,2-H migration to form the (*Z*)- and (*E*)-β-chlorostyrenes. The rate for the 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 [pyridine] = 0. From such measurements, performed at various temperatures, the kinetic parameters E_i = 4.5 kcal/mol and $A_i = 10^{11.1}$ s^{-1} are obtained. LFP of **1** in the absence of pyridine produces a transient absorption (280–330 nm) assigned to benzylchlorocarbene. Monitoring the carbene decay directly at 310 nm over the same temperature range gives similar values: E_i = 4.8 kcal/mol and $A_i = 10^{11.3}$ s^{-1}. Three independent methods—LFP, products ratios (*Z/E* and cyclopropane/chlorostyrenes)—yield a single value, (6.2 ± 0.2) 10^8 M^{-1} s^{-1} for k_t, the rate constant for the addition of benzylchlorocarbene to tetramethylethylene. These results are consistent with a mechanism involving the formation of a complex between benzylchlorocarbene and tetramethylethylene.

The most common rearrangement reaction of alkyl-substituted carbenes is the migration of a hydrogen atom to the carbene center which affords an alkene. Theoretical calculations have deduced



$$R{-}\underset{\displaystyle H}{\underset{|}{CH}}{-}\ddot{C}{-}X \longrightarrow R{-}CH{=}CHX$$

energy barriers to this rearrangement ranging from 0 to 27 kcal/mol.[1-6] The original zero value,[2] obtained by the semiempirical MINDO method, was considered unreliable due to the known deficiency of MINDO in favoring cyclic structures. Ab initio methods gave large values,[1,4] but more sophisticated calculations, involving polarized functions and correlation effects, reduced the value of the energy barrier to 2.1 kcal/mol.[5]

Experimentally, work on 1-aryl-2-diazopropanes[7] and examination of the vibrational structure of vinylidene photoelectron spectrum[8] has produced evidence of a definite barrier for 1,2-H migration, even though no value was assigned. Recently, the products derived from the thermolysis of 4-diazirinopentanoic acid gave an estimate of 1.1 ± 1 kcal/mol for the height of the barrier to 1,2-H shift in a dialkylcarbene.[9] By examining the competition between inter- and intramolecular reactions of halocarbenes, Liu and Subramanian[10,11] estimated the barrier to be 6.4 and 4.7 kcal/mol in Ph–CH_2–$\ddot{C}$–Cl and Ph–CH_2–$\ddot{C}$–Br, respectively. Although the estimated values may have errors of ±2 kcal/mol, this latter work provides a valuable beginning for further insight into factors which control the intramolecular rearrangement.

Direct measurement, by laser flash photolysis, of the rate of H migration as a function of temperature seems quite difficult in the case of benzyl- and alkylhalocarbenes because, unlike arylhalocarbenes which are easily detected,[12] these species do not absorb with a high extinction coefficient in an easily accessible part of the spectrum. The "pyridine probe" technique[13] presents

---

[†] Dedicated to Professor Wolfgang Kirmse on the occasion of his 60th birthday.

[‡] On leave from the University of Prince Edward Island (1988–1989), Charlottetown, Prince Edward Island, Canada, C1A 4P3.

(1) Schaefer, H. F., III *Acc. Chem. Res.* **1979**, *12*, 288.

(2) Bodar, N.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9103. Kyba, E. P. *J. Am. Chem. Soc.* **1977**, *99*, 8330.

(3) Frenking, G.; Schmidt, J. *Tetrahedron* **1984**, *40*, 2123.

(4) Altman, J. A.; Csizmadia, I. G.; Yates, K. *J. Am. Chem. Soc.* **1974**, *96*, 4196. Altman, J. A.; Csizmadia, I. G.; Yates, K. *J. Am. Chem. Soc.* **1975**, *97*, 5217.

(5) Nobes, R. H.; Radom, L.; Rodwell, W. R. *Chem. Phys. Lett.* **1980**, *74*, 269.

(6) Raghavachari, K.; Frisch, M. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *85*, 145.

(7) Su, D. T. T.; Thornton, E. R. *J. Am. Chem. Soc.* **1978**, *100*, 1872.

(8) Burnett, S. M.; Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *Chem. Phys. Lett.* **1983**, *100*, 124.

(9) Stevens, I. D. R.; Liu, M. T. H.; Soundararajan, N.; Paike, N. *Tetrahedron Lett.* **1989**, *30*, 481.

(10) Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 982.

(11) Liu, M. T. H.; Subramanian, R. *J. Phys. Chem.* **1986**, *90*, 75.

(12) (a) Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1987. (b) Moss, R. A.; Lawrynowicz, W.; Turro, N. J.; Gould, I. R.; Cha, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7028.

0002-7863/90/1512-3915$02.50/0

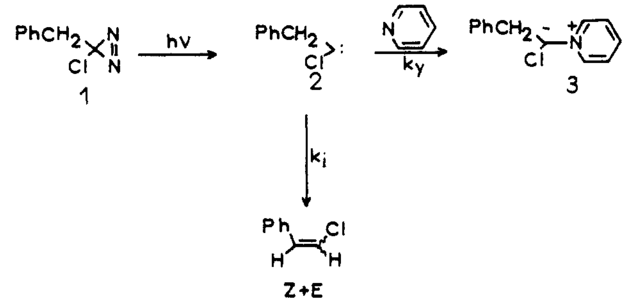
Table I. Rate Constants for 1,2-H Shift in Benzylchlorocarbene and for the Formation of the Pyridinium Ylide

temp (°C)	1	14	25	31
k_y (10^9 M^{-1} s^{-1})^a	7.94 ± 0.56	7.89 ± 0.30	7.57 ± 0.51	7.78 ± 0.13
k_i (10^7 s^{-1})^a	3.06 ± 0.14	4.80 ± 0.05	6.06 ± 0.10	7.00 ± 0.10

temp (°C)	−4	5	18	24	34
k_i (10^7 s^{-1})^b	2.22 ± 0.1	2.94 ± 0.1	4.65 ± 0.2	5.41 ± 0.2	6.54 ± 0.3

[a] From the growth of the ylide absorption, monitored at 370 nm. [b] From the decay of the carbene absorption, monitored at 310 nm.

Scheme I



a new strategy for the study of these "invisible" carbenes. We have recently reported the measurement by this technique of the rate constant of 1,2-H migration in benzylbromocarbene at room temperature.[14]

We now wish to report the first determination of the activation energy for this process in benzylchlorocarbene as well as the first observation of an absorption band of this carbene in solution, at room temperature. In addition, the mechanism for cycloaddition of this carbene to alkenes is discussed on the basis of a comparison between new data obtained by flash photolysis and results previously obtained from product analysis after continuous irradiation.[10]

Experimental Section

3-Chloro-3-benzyldiazirine, **1**, was prepared by Graham's method[15] and purified by chromatography on 60–200 mesh silica gel. Pyridine was distilled over CaH_2 which has been shown to be superior to other desiccants, including sodium.[16] The laser flash photolysis setup uses a crossed-beam arrangement. The sample in a 10 × 10 mm cell was excited at 355 nm by single light pulses (200 ps; 5–30 mJ) provided by a frequency tripled mode-locked Nd-YAG laser (Quantel). The detection system (pulsed Xe-arc, monochromator, photomultiplier, and Tektronix 7912 transient recorder) has a response time around 4 ns. GLC analyses of absolute yields of chlorostyrene were performed on a Varian Vista 6000 gas chromatograph fitted with a 6 ft × 0.125 in. stainless steel column packed with CSP 20M and using a flame ionization detector. Peak areas were integrated with a Hewlett-Packard 3390A recorder.

Results and Discussion

Ylide Formation and H Migration. Laser flash photolysis of **1** in isooctane in the presence of pyridine produces a transient species with an absorption band peaking around 380 nm. This transient is not present in the absence of pyridine and is attributed to pyridinium ylide **3**. The rate of formation of this ylide allows us to measure the absolute rate constant for the 1,2-H migration in benzylchlorocarbene, **2**. Plots of the observed pseudo-first-order rate constants for the growth of the absorption at 370 nm vs [pyridine] are linear (Figure 1). Their slope gives the rate constant for reaction of the carbene with pyridine, k_y, and the intercept (extrapolation to [pyridine] = 0) yields the rate constant for 1,2-H shift, k_i. The values of k_y and k_i measured by this method at four temperatures in the 0–31 °C range are given in Table I. Within experimental error, the rate constant for ylide formation is diffusion controlled, and its activation energy is approximately zero. The plot of $\log(k_i)$ vs $1/T$ (Figure 2) is linear and gives $E_i = 4.5 \pm 0.3$ kcal/mol and $A_i = 10^{(11.1 \pm 0.2)}$ s^{-1}. These values are in excellent agreement with the E_i and A_i values estimated earlier from the competition between inter- and intramolecular reactions.[10]

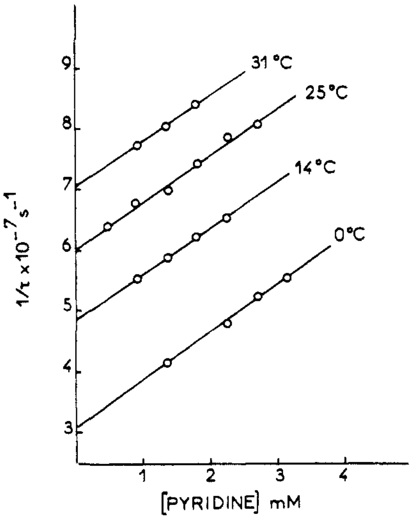


Figure 1. Reciprocal lifetime of benzylchlorocarbene, as determined from the growth of the ylide absorption at 370 nm, $1/\tau$ vs [pyridine] at various temperatures in isooctane. The values of the rate constant for 1,2-H migration are given by the extrapolated intercepts.

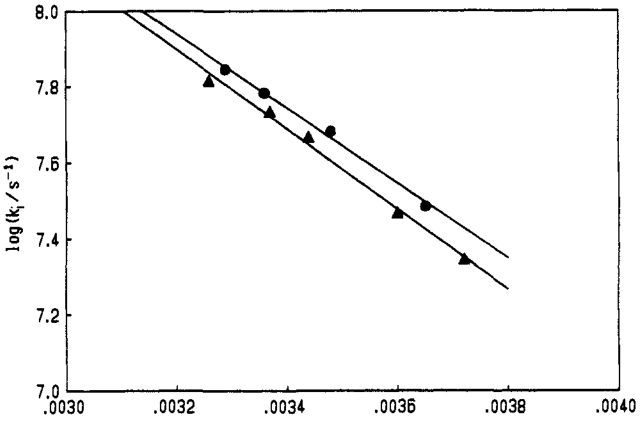


Figure 2. Arrhenius plots of the rate constant for 1,2-H migration measured by (●) the pyridine probe technique and (▲) by direct observation of the carbene at 310 nm.

GC analysis of the products formed after complete photolysis of three solutions with concentrations of added pyridine equal to zero, 0.0045 and 0.009 M, and with chlorobenzene as an internal standard, indicates that (i) pyridine has a dramatic influence on the Z/E ratio of the chlorostyrene isomers which changes from 0.2 to 0.37 to 0.42, respectively. (ii) the global yields of chlorostyrenes in the three solutions are identical within the experimental errors and equal to 90% in the presence of pyridine. These results are not compatible with a mechanistic scheme where the ylide formation would be irreversible, and the 1,2-H shift would occur only from the free carbene since the yield of chlorostyrenes, calculated with the values of k_i and k_y, would be reduced from 1 to 0.6 and 0.43, respectively, in the presence of pyridine. Thus one must consider either that the 1,2-H shift can occur in the ylide or that the ylide formation is reversible.

---

(13) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.

(14) Bonneau, R.; Liu, M. T. H.; Suresh, R. V. *J. Phys. Chem.* **1989**, *93*, 4802.

(15) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(16) Burfield, D. R.; Smithers, R. H.; Tan, A. S. C. *J. Org. Chem.* **1981**, *46*, 629.

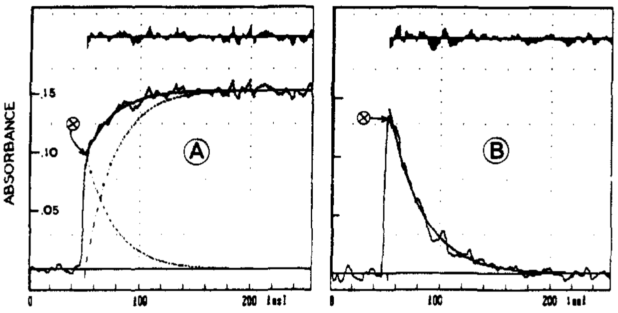


Figure 3. Transient absorbance signal obtained at 280 nm (A) and 310 nm (B) by LFP of diazirine **1** in isooctane at ≈15 °C: sweep rate, 500 ns = 512 channels (only 256 channels are represented here), and laser pulse, on channel 48. The "4-ns spectrum" in Figure 5 is obtained from the point indicated on channel 52. The 280-nm trace may be analyzed as the sum of the absorptions of the carbene **2** and of the β-chlorostyrene, respectively, decaying and growing with a first-order kinetics (τ = 26 ns). The 310-nm trace can be fitted with a single exponential decay ($\tau \approx$ 28 ns). Figure 3 (parts A and B) has the same unit on the vertical axis.

Both hypotheses are consistent with the fact that the absorption of **3** at 380 nm decayed slowly with a lifetime around 0.1 ms in isooctane at 25 °C, whereas certain pyridinium ylides are known to be rather stable and even isolable.[17] This lifetime depends on the pyridine concentration and decreases when [pyridine] increases. This is the opposite of what would occur if a simple equilibrium existed between the carbene, the pyridine, and the ylide. Then, increasing the [pyridine] would shift the equilibrium toward the "stable" ylide and would increase the lifetime.

One must therefore consider that the 1,2-H shift occurs in the ylide, possibly assisted by the pyridine itself because H transfer catalyzed by organic bases is a well-known reaction.[18] Indeed, a plot of the reciprocal lifetime of **3** vs [pyridine] yields a rate constant $k = (3.37 \pm 0.13) \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$ for the quenching of **3** by pyridine. Similarly, 2,6-di-*tert*-butylpyridine, an organic base which does not form an ylide with **2**, quenches ylide **3** with a rate constant $k = (8.49 \pm 0.57) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$.

The changes in the Z/E ratio as a function of [pyridine] are easily rationalized by assuming that the two types of 1,2-H transfer (in the free carbene and in the ylide) produce the (Z)- and (E)-chlorostyrene isomers with a different specificity.

Direct Observation of the Benzylchlorocarbene. The UV spectrum of a solution of diazirine **1** in isooctane consists of a structured absorption band in the 310–370-nm region, with low extinction coefficients, and another one in the 220–280-nm range, very poorly structured, broad, and intense. Transient absorption measurements are possible in the window 280–330 nm between these two bands. In the 300–330-nm region, a transient absorption appears within the response time of our analytical system (i.e., within the 4 ns following the 200-ps excitation pulse) and decays with a lifetime around 20 ns at room temperature (Figure 3B). In the 275–285-nm region, the changes in the absorbance are characterized by an "instantaneous" jump of the absorption followed by a growth, with a first-order rate constant around 20 ns (Figure 3A). At 290–295-nm, the absorption remains nearly constant after the initial jump. The transient absorption is clearly due to the contribution of two species. The second one is formed, at least partially, from the first one. The absorption spectrum of the second species is derived from the transient absorptions measured after the complete decay of the first species (i.e., 100 ns after the excitation) since the correction which accounts for the diazirine bleaching is negligible. As shown in Figure 5, this spectrum is identical with the absorption spectrum of β-chlorostyrene recorded on a conventional spectrophotometer after complete photolysis of the diazirine solution with 300–400-nm light. Therefore the second species is identified to be β-chlorostyrene. The first species which has a broad absorption over the 280–330-nm region is assigned to benzylchlorocarbene, **2**. This assignment is suggested by the good agreement between the time constants for (i) its decay, measured at 305 nm, (ii) the formation of β-chlorostyrene, measured at 280 nm, and (iii) the growth of the pyridinium ylide, measured at 370 nm and extrapolated to [pyridine] = 0.

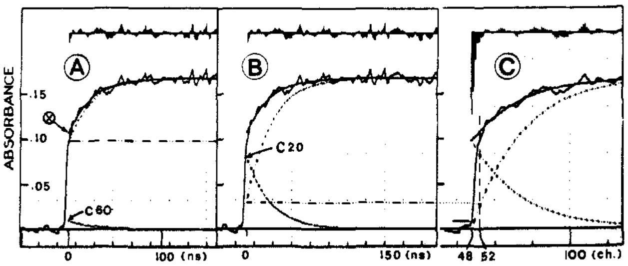


Figure 4. (A–B) Alternative analyses of the 280-nm trace presented in Figure 3A, with τ = 26 ns in all cases but with two different estimates for the amount of chlorostyrene formed during the 4 ns following the excitation: 60% of the final amount in A and 20% in B as represented by the horizontal dashed lines. The corresponding values of the carbene absorption, indicated as C60 and C20, are used to draw the "corrected spectra" in Figure 5. The expanded graph (C) shows that the rearrangement of the carbene during the response time of the detection system may be responsible for the formation of ≈20% of the chlorostyrenes. The residues, indicated on the upper part of the graph, are consistent with an "instantaneous" jump of the signal convoluted with a 4-ns response time.

The absorption spectrum of the benzylchlorocarbene, **2**, is derived from the transient absorptions measured immediately (≈4 ns) after the excitation and after subtraction of the absorption due to the amount of β-chlorostyrene formed during the first 4 ns. Assuming that the carbene formation is very fast (<1 ns), it can be calculated, from $1 - \exp(-t/\tau)$ with $t \approx 4$ ns and $\tau \approx 20$ ns, that about 20% of the carbene can rearrange to chlorostyrene during the response time of our analytical system. If the β-chlorostyrene is formed from the carbene only, the absorption spectrum of the carbene is obtained by subtracting 20% of the "100-ns spectrum" from the "4-ns spectrum". This process gives the corrected carbene spectrum shown in Figure 5 and the kinetic analysis of the trace recorded at 280 nm shown in Figure 4 (B and C).

However, it is kinetically impossible to distinguish between the previous analysis and a situation where some β-chlorostyrene would be formed within less than 4 ns via a noncarbenic pathway involving, for instance, a diazo intermediate. In Figure 4A, the amount of chlorostyrene formed after 4 ns is assumed to be ≈60% of the final value, and the resulting curve fitting is strictly equivalent to the one given in Figure 4B. This would correspond to 50% of β-chlorostyrene being formed via a noncarbenic route and 50% via the carbene, 20% of the latter 50% being formed within 4 ns. The resulting absorption spectrum of the carbene, calculated with a correction factor (fraction of the chlorostyrene spectrum to be subtracted from the "4 ns spectrum") equal to 60%, is shown in Figure 5. The correction factor cannot exceed 60% since this would give a negative absorption for the carbene at 280 nm. It should be kept below 35% to avoid the appearance of an unexpected structure on the blue side of the resulting carbene absorption band. Since a correction factor of 32% would correspond to ≈15% of β-chlorostyrene being formed from a noncarbenic source, a noncarbenic route should be only a minor pathway, if it exists.

The temperature dependence of k_i was determined by direct observation, at 310 nm, of the decay of the carbene in the −4 to 34 °C temperature range. The results are given in Table I and the Arrhenius plot in Figure 2. The kinetic parameters given by a least-squares analysis, $E_i = 4.83 \pm 0.24$ kcal/mol and $A_i = 10^{(11.28 \pm 0.20)}\ \mathrm{s^{-1}}$, are nearly identical with those derived from the pyridine technique.

Finally, the rate constant for the quenching of the carbene **2** by tetramethylethylene, TME, in isooctane to form cyclopropane has been determined by measuring the rate of decay of the carbene

---

[17] Zugravescu, I.; Petrovanu, M. *N-Ylid Chemistry*; McGraw-Hill: New York, NY, 1976.

[18] Wubbles, G. G. *Acc. Chem. Res.* **1983**, *16*, 285.

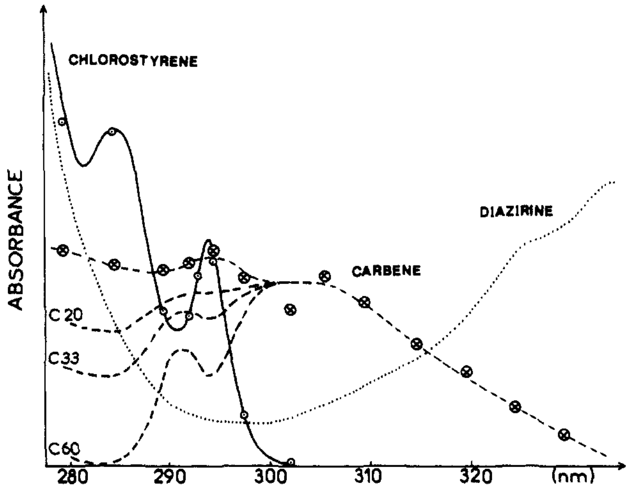


Figure 5. Absorption spectra of β-chlorostyrene (solid line) and of diazirine **1** in isooctane (dotted line) recorded on a conventional spectrophotometer, and transient absorptions measured in LFP 4 ns (⊗) and 100 ns (⊙) after the excitation. The dashed lines labeled C20, C33, and C60 are the carbene absorption spectrum obtained after correction of the "4-ns spectrum" (dashed line through the (⊗)) by 20, 33, and 60% of the β-chlorostyrene spectrum.

absorption at 310 nm, $k_d = k_i + k_q[\mathrm{TME}]$. Least-squares analysis of measurements for four different concentrations of TME ranging from 4 to 25 mM gave $k_q = (7.9 \pm 0.7) \times 10^8$ M^{-1} s^{-1} at 22 °C. Each measurement consists of an average of five determinations. The intercept yielded a value of 5.1×10^7 s^{-1} for k_i. This is in agreement with the lifetime of carbene **2**, τ = 20 ns at 22 °C, measured both at 300 or 310 nm.

Mechanism for Cyclopropanation. The relative reactivity of benzylchlorocarbene toward various alkenes has previously been evaluated from measurements by GC of the amounts of cyclopropane and styrene products formed after complete photolysis by continuous irradiation. Some interesting features of the carbene, such as its ambiphilicity,[19] have been established by this method. A mechanistic scheme, based on the Turro and Moss model[12] and involving a carbene–olefin complex (see Scheme II), has been proposed by Liu[10] in order to rationalize the variations of the (Z/E) and [chlorostyrenes]/[cyclopropane] ratios as a function of [alkene] and temperature. Two alternative mechanisms could explain the linear plot for the ratio [chlorostyrenes]/[cyclopropane] vs 1/[olefin] and a change in the Z/E ratio. According to Warner,[20a] an excited carbene, with a lifetime too short for being quenched by olefins, would produce a fraction of the chlorostyrenes with a Z/E ratio that differs from the one for the chlorostyrenes formed from the "relaxed carbene". Platz[20b] proposed that the excited diazirine leads to a mixture of carbene and diazo compound, both of which could give the chlorostyrenes (but with different Z/E ratios), whereas only the carbene could add to the olefin. However, the plots of [chlorostyrenes]/[cyclopropane] vs 1/[alkene] obtained for diazirine **1** and various alkenes have different, but positive, intercepts,[10,19] (Figure 6) whereas both the "excited carbene model" and the "diazo mechanism" predict the intercept to be independent of the nature of the alkene and to be determined only by the properties of the excited carbene or diazirine. Bonneau, Liu, and Suresh[14] have already pointed out that this observation strongly supports the "complex model" which predicts (or is compatible with) an intercept depending on the nature of the alkene.

The availability of the absolute value of k_i and the possibility of determining some other rate constant(s) by LFP prompted us to reexamine the addition of benzylchlorocarbene to tetramethylethylene (TME). With the "complex model" and the notations represented in Scheme II, the steady-state approximation applied to the system "carbene + TME" gives

$$[\text{styrene}]/[\text{cyclopropane}] = (k_i'/k_2) + (k_i/k_t) \times (1/[\text{TME}])$$

where $k_t = k_1k_2/(k_2 + k_i' + k_{-1})$.

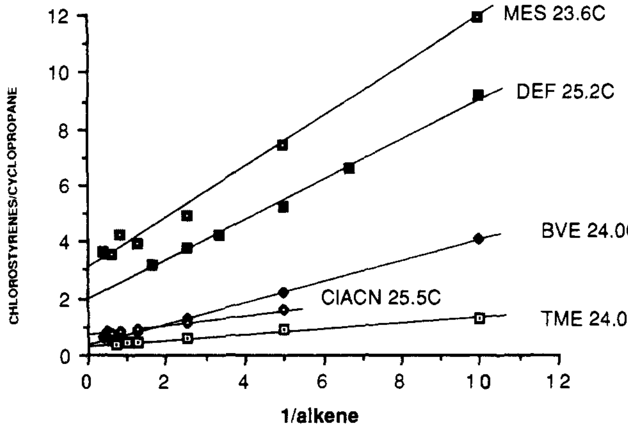
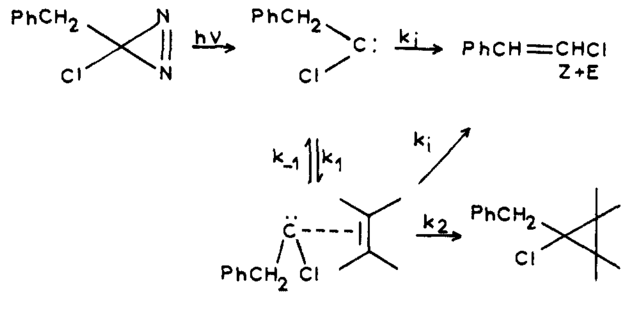


Figure 6. Plots of chlorostyrenes/cyclopropane vs 1/alkene for tetramethylethylene (TME), α-chloroacylonitrile (ClACN), butyl vinyl ether (BVE), diethyl fumarate (DEF), and diethyl mesaconate (MES). Data taken from refs 10 and 19.

Scheme II



Plotting the ratio [styrene]/[cyclopropane] vs 1/[TME] from data in ref 10 yields an intercept of 0.34 and a slope of 0.096 from which, with $k_i = 6 \times 10^7$ s^{-1}, one gets

$$k_t = 6.25 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

In flash photolysis experiments, when a constant amount of pyridine is used, the addition of olefin causes a decrease of the amount of ylide **3** because the cycloaddition between the carbene and the olefin competes with the ylide formation. The amount of ylide is evaluated by the absorbance at 370 nm measured a few tens of nanoseconds after the excitation pulse, i.e., after a delay long enough to get a complete decay of the carbene but short enough to enable the ylide, which has a lifetime of several hundreds of microseconds, to be considered stable. A quantitative analysis of this effect gives a way to measure the rate constant for reaction of the carbene with the added olefin.

The steady-state approximation applied to Scheme II (with an additional reaction for the formation of the pyridinium ylide) gives the following expression for the quantum yield of formation of the ylide:

$$\phi_y = k_y[\text{pyr}]/(k_i + k_y[\text{pyr}] + k_1R[\text{TME}]) \text{ with } R = (k_2 + k_i')/(k_2 + k_i' + k_{-1})$$

Since it is not clear that the steady-state approximation may be used to get the analytical expression of the quantum yield of formation of a species in a laser flash experiment, ϕ_y was also calculated by using the dynamic model and the equations derived by Birks[21] for the analysis of the excimer problem. One gets exactly the same expression, without any approximation.

With $\phi_y{}^\circ = k_y[\text{pyr}]/(k_i + k_y[\text{pyr}])$ being the yield of ylide formation in the absence of olefin

$$\phi_y{}^\circ/\phi_y = 1 + k_1R[\text{TME}]/(k_i + k_y[\text{pyr}])$$

---

[19] Liu, M. T. H.; Suresh, R. V.; Soundararajan, N.; Vessey, E. G. *J. Chem. Soc., Chem. Commun.* **1989**, 12.

[20] (a) Warner, P. M. *Tetrahedron Lett.* **1984**, *25*, 4211. (b) See footnote 23 in the following: Jackson, J. E.; Soundararajan, N.; White, W.; Liu, M. T. H.; Bonneau, R.; Platz, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 6874.

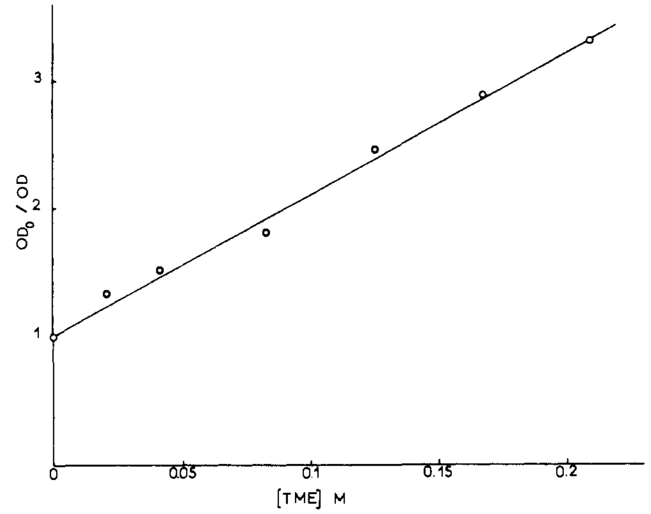


Figure 7. Stern–Volmer plot for the quenching of the formation of the pyridinium ylide by added TME: solvent, isooctane; temperature, 25 °C; [pyr] = 2 mM.

Since the absorbance measured at 370 nm is proportional to the yield of ylide formation, the slope of the straight line in Figure 7 obtained by plotting OD_0/OD vs [TME] is equal to $k_1R/(k_i + k_y[\mathrm{pyr}])$. With the known values of k_i, k_y, and [pyr], one gets $k_1R = 8 \times 10^8$ M^{-1} s^{-1}. From the expressions of R and k_t, it follows that $k_1R/k_t = (k_2 + k_i')/k_2 = 1.34$ since $k_i' = 0.34\ k_2$ was obtained from the intercept of the plot [styrene]/[cyclopropane] vs 1/[TME]. Thus, the laser flash photolysis method gives

$$k_t = 5.97 \times 10^8\ M^{-1}\ s^{-1}$$

In addition, assuming that the 1,2-H shift produces the Z and E isomers of β-chlorostyrene in a Z/E ratio = α from the "free carbene", whereas this ratio would be β for the chlorostyrenes formed from the "carbene–olefin complex", the mechanism presented in Scheme II allows the changes of the Z/E ratio as a function of [TME] to be accounted for.

With $\phi_s = k_i/(k_i + k_t[\mathrm{TME}])$ being the yield of β-chlorostyrene formed from the carbene, the amounts of Z and E isomers formed in this way are $\phi_s\alpha/(\alpha + 1)$ and $\phi_s/(\alpha + 1)$, respectively.

Similarly, with $R'' = k_i'/(k_2 + k_i' + k_{-t})$, the yield of β-chlorostyrene formed from the complex is $\phi_s' = k_1R''[\mathrm{TME}]/(k_i + k_t[\mathrm{TME}])$ and the amounts of Z and E isomers produced by this second way are respectively $\phi_s'\beta/(\beta + 1)$ and $\phi_s'/(\beta + 1)$. Then,

$$Z/E = \{[\phi_s\alpha/(\alpha + 1)] + [\phi_s'\beta/(\beta + 1)]\}/\{[\phi_s/(\alpha + 1)] + [\phi_s'/(\beta + 1)]\}$$

This rearranges to

$$1/(Z/E - \alpha) = 1/(\beta - \alpha) + k_i(\beta + 1)/\{(\beta - \alpha)(\alpha + 1)k_1R''[\mathrm{TME}]\}$$

With α = 0.20, the plot of $1/(Z/E - \alpha)$ vs 1/[TME] indeed gives a straight line (Figure 8) with an intercept $1/(\beta - \alpha) = 1.58$, from which we derive β = 0.83 and a slope equal to 0.665 yielding $k_1R''/k_i = 3.64$. Since $k_1R''/k_t = k_i'/k_2 = 0.34$, this method gives

$$k_t = 10.7k_i = 6.42 \times 10^8\ M^{-1}\ s^{-1}$$

Three independent kinetic analyses, based on the variations of

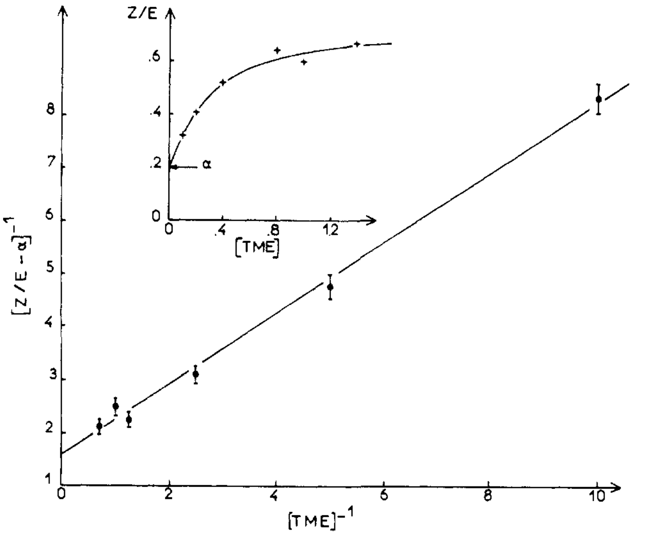


Figure 8. Effect of [TME] on the distribution of Z and E isomers of β-chlorostyrene.

independent parameters ([ylide], [styrene]/[cyclopropane], and Z/E ratios) measured under quite different conditions (after continuous irradiation and in laser flash photolysis), give a single value of $k_t = 6.2 \pm 0.2 \times 10^8$ M^{-1} s^{-1}. This fact strongly supports the proposed mechanistic scheme and the existence of a carbene–alkene complex from which the 1,2-H shift can compete with cyclopropanation.

The notion of a reversibly formed carbene–olefin complex was introduced by Turro and Moss[12] to account for the negative activation energies observed for the addition of Ph–C–Cl to trimethyl- and tetramethylethylene. However, Houk and Rondan[22] have argued 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. Their theoretical calculations provided no evidence for a carbene–alkene complex.

In our laser flash photolysis experiments, we were unable to observe any transient absorption which could be assigned to this complex, but this is not an argument against the complex hypothesis. The absorption spectrum of the complex may be similar to that of the free carbene if the complex is weakly bonded or its extinction coefficient may be low in the spectral range accessible to analysis. Furthermore, with the low TME concentration (25 mM) used in this study, it is possible to show that the concentration of the complex is always less than 6% of the initial carbene concentration.

Thus, neither time-resolved spectroscopy nor activation energy measurements are able to prove (or disprove) the existence of this complex. But its existence is compatible with all the kinetic and spectroscopic results obtained by laser flash photolysis and is strongly supported by the variations of the relative amounts of the various products of the reaction measured under continuous irradiation.

Registry No. 1, 88211-05-6; benzylchlorocarbene, 88211-07-8; pyridine, 110-86-1; tetramethylethylene, 563-79-1.

---

[21] Birks, J. B. *Photophysics of Aromatics Molecules*; Birks, J. B., Ed.; Wiley-Interscience: London, England, 1970; pp 303–305.

[22] Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291 and 4293.