J. Phys. Chem. A **2000,** *104,* 4115−4120

Kinetic and Spectroscopic Properties of Carbene−Diazirine Ylides

Roland Bonneau*

U.M.R. 5803, Université de Bordeaux I, 33405 Talence Cedex, France

Michael T. H. Liu

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

Received: October 18, 1999; In Final Form: February 14, 2000

The formation of a metastable carbene−diazirine ylide (CDY), characterized by an UV absorption spectrum in the range of 270−290 nm and yielding azine by rearrangement, is shown to be a general process in the photolysis of diazirines. However, the yield of formation and the lifetime of CDY greatly depend on the system considered. The decreasing value of the rate constant of the reaction, carbene + diazirine → CDY, from $\sim 10^9$ M^{-1} s^{-1} for singlet dialkylcarbenes, Ad: (adamantylidene) and BCN: (bicyclo[3.3.1]non-9-ylidene), to $\sim 10^8$ M^{-1} s^{-1} for benzylchlorocarbene and to $\sim 10^6$ M^{-1} s^{-1} for cyclopropyl and phenylchlorocarbenes, reflects the decreasing reactivity of these carbenes. The lifetime of these ylides is determined by the value of the activation energy barrier for their rearrangement to azine, $E_a \approx 15.5$ kcal/mol for dialkylcarbenes, ≈ 11.5 kcal/mol for alkylchlorocarbenes, and <10 kcal/mol for phenylchlorocarbene. This decrease of E_a is related to the strong stabilization of the azine when proceeding from $CR_2{=}N{-}N{=}CR_2$ to $Ph{-}CCl{=}N{-}N{=}CCl{-}Ph$. Another mechanism for the formation of azine, by a second-order reaction of the diazo isomer of the diazirine, is clearly identified in the case of photolysis of the BCN(N_2) diazirine.

1. Introduction

During the past decade, many rate constants and kinetic parameters of intramolecular and intermolecular reactions of carbenes have been measured, mainly by laser flash photolysis (LFP) and, in a few cases, by other time-resolved techniques such as photoacoustic calorimetry (PAC).[1] In almost all cases, the carbene was produced by photolysis of a diazirine. Although it is a well-known fact that carbenes react with diazirines to yield azines, the rate constant of this reaction (k_r) has not been measured systematically, and the contribution of this reaction to the measured rate of decay of the carbene has been often neglected. This omission seemed reasonable because the few measurements[2] of k_r gave values in the range of 10^6−10^8 M^{-1} s^{-1} so that, with diazirine concentrations in the range 1−10 mM, the product k_r[diazirine] is negligible when compared to the reciprocal of the measured lifetimes which, in most cases, are in the range of 10−100 ns.

Recently we discovered that adamantylidene, Ad:, reacts with its parent diazirine with a rate constant around 3×10^9 M^{-1} s^{-1}, larger by 2 or 3 orders of magnitude than the previously estimated values of k_{az}, to give a carbene−diazirine ylide (CDY) which shows an intense UV absorption in the 290 nm region and gives the azine via a reaction decelerated by a 15 kcal/mol activation energy.[3] The structure of this ylide, deduced from theoretical calculations,[4] is demonstrated in Scheme 1.

Surprisingly, this kind of ylide has never been reported in previous studies, although in almost every case, the 290 nm region was “clear” from any intense absorption band that could have prevented investigation in this region. For instance, in the studies of cyclopropylchlorocarbene (CpClC:), produced by photolysis of the 3-cyclopropyl-3-chlorodiazirine, the spectral region below 300 nm was investigated by Moss[5] because the carbene absorption was observed in the 260−240 nm range. However, no CDY was reported, despite the fact that CpClC: has a lifetime that is longer than 1 μs at room temperature, comparable to that of Ad:. Even further, Moss and co-workers have stated that, for this system, “product studies exclude complications due to azine formation”.[6]

This anomaly raises several questions. Is adamantylidene so much different from the previously investigated carbenes, and is there a general difference between alkylchlorocarbenes and dialkylcarbenes? Does a CDY also exist in the previously studied systems, and if so, why was this species never reported? Does the formation of azine proceed exclusively via a CDY? Finally, are rearrangement reactions (e.g., 1,2-H shift) possible within the ylide, which would affect the results of mechanistic studies of intra- and intermolecular reactions of carbenes?

This study reports the reaction of several carbenes, all of them with an expected singlet ground state, with their parent diazirine: (i) bicyclo[3.3.1]non-9-ylidene, a dialkylcarbene closely related to Ad:, (ii) benzylchlorocarbene and cyclopropylchlorocarbene, two alkylchlorocarbenes suffering, respectively, a fast 1,2-H shift and a slow 1,2-C rearrangement, and (iii) phenylchlorocarbene, an arylchlorocarbene in which no intramolecular rearrangement reaction is possible. These results satisfy most, if not all, of the above questions.

2. Experimental Section

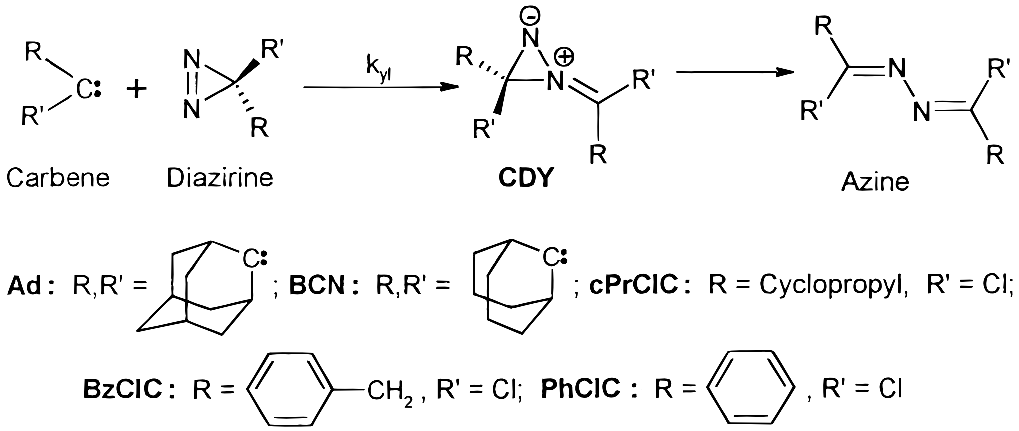
We prepared bicyclo[3.3.1]nonan-9-diazirine by oxidation of the diaziridine and it was characterized by ^{13}C and ^1H NMR: C[diazirine] δ 34.1; C_1 δ 21.9, H_{ab} δ 1.7(2), δ 1.45(2); C_2 δ 29.5, H_{cd} δ 1.8(4), δ 1.4(4); C_3 δ 34.7, H_e δ 0.35(2). We obtained other diazirines by oxidation of the corresponding amidines by NaOCl according to the Graham’s procedure.[7] We

---

* Corresponding author. E-mail: bonneau@cribx1.u-bordeaux.fr.

10.1021/jp993711w CCC: $19.00

SCHEME 1



used isooctane as solvent, because (i) most of the previous studies have been performed in this solvent, (ii) it is transparent in the UV region, (iii) compared to other alkanes, its reactivity with alkylchlorocarbenes is minimized, and (iv) fluid solutions can be studied on a large temperature range (from −105 to +95 °C).

The LFP system uses a frequency-tripled, mode-locked Nd: YAG laser (Quantel) as excitation source (200 ps, 355 nm, 20 mJ/pulse), a crossed beam arrangement (optical paths: 2 mm for excitation, 10 mm for analysis), and a detection system with a 5−10 ns response time. Data have been collected on a Tektronix 7912AD transient digitizer (for the short-lived transients) or a digital oscilloscope, Tektronix TDS 620B (for the long-lived species). We obtained absorption spectra of transient species "point by point" by successive measurements of the transient absorbance at various wavelengths.

We measured the absorption spectra of species with a lifetime in excess of a few seconds on a photodiode array spectrophotometer (HP 8452A) recording a spectrum in the range of 200−800 nm, with a 2 nm/point resolution, within 1 s (0.1 s possible). Kinetic information can be obtained by recording the spectrum (or the absorbance at selected wavelengths) at regular time intervals. Using a homemade accessory, the sample can be cooled to −100 °C by cold N_2 gas flowing around the cell (1 or 10 mm path length), the temperature being measured by an inox clad thermocouple immersed in the solution. We photolyzed the sample, within the low-temperature accessory, during a short period of time (1−10 s) by a frequency-tripled Nd:YAG laser (BMI, 15 ns, 30 mJ/pulse, 10 Hz). We used a flow of N_2 gas bubbling in the solution during the irradiation to homogenize the sample and then stopped it before the recording of the spectra.

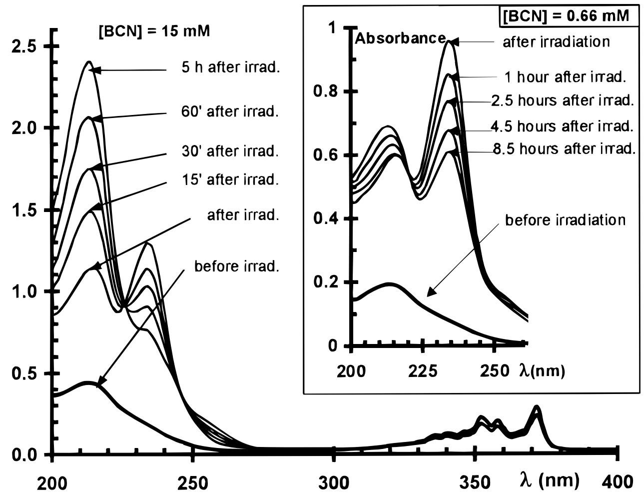


Figure 1. Absorption spectra of a solution of BCN diazirine in isooctane at room temperature, before and after irradiation at 355 nm. Main figure: 1 mm optical path, [diazirine] = 15.5 mM. Inset: 10 mm optical path, [diazirine] = 0.66 mM. Notice the slower decay of the diazo at 234 nm and the lower yield of formation of azine at 214 nm.

3. Results

3.1. Bicyclo[3.3.1]nonan-9-diazirine (BCN(N_2)). After photolysis at room temperature (≈25 °C) of diluted solutions (≈0.66 mM) of this diazirine in a 10 mm cell by a few laser shots at 355 nm, the concentration of diazirine is decreased by about 0.2 mM and two new absorption bands appear: the first one at 234 nm ($\Delta A_{234} = 0.877$) is due to the diazo and the second at 214 nm ($\Delta A_{214} = 0.4$) is mainly due to the azine, but the diazo also contributes for at least 0.1 to this increase of A_{214}. Assuming that the absorption coefficients are $\epsilon_{234} \approx 8000$ M^{-1} cm^{-1} for the diazo and $\epsilon_{214} \approx 22\,500$ M^{-1} cm^{-1} for the azine, as in the Ad:Ad(N_2) system, the yields of formation of the diazo and of the azine are ≈48% and 4%, respectively. The thermal decay of the diazo is slow (only one-third disappeared after 4 h) and little azine is produced during this decay. (See inset in Figure 1.)

Photolysis of a concentrated solution (15.5 mM) in a 1 mm cell under similar conditions produces a 2.55 mM decrease of the concentration of diazirine and a growth of the absorption bands at 234 nm ($\Delta A_{234} = 1.11$) and at 214 nm ($\Delta A_{214} = 0.697$). (See Figure 1.) With the same assumptions as above on the values of ϵ_{234} and ϵ_{214} and on the overlap of the azine and diazo absorptions, the yield of formation of the diazo is approximately 45%, close to the above value, whereas the yield of formation of the azine is around 10%, more than double the value obtained in diluted solution. The thermal decay of the diazo proceeds at a much faster rate than in diluted solution, and a significant amount of azine is produced during this decay. Based on the amplitude of the increase of the absorbance at 214 nm, approximately 0.6 mM azine is formed during the decay of 1.12 mM diazo. This suggests that most of the azine is formed by a diazo + diazo reaction, a hypothesis supported by the fact that diazirine is not consumed during the decay of the diazo.

Photolysis of concentrated solutions (≈20 mM, 1 mm cell) at low temperatures (between −20 and −60 °C) gives quite different results (see Figure 2). Immediately after irradiation, the absorption of azine, in the 200−220 nm range, is (almost)

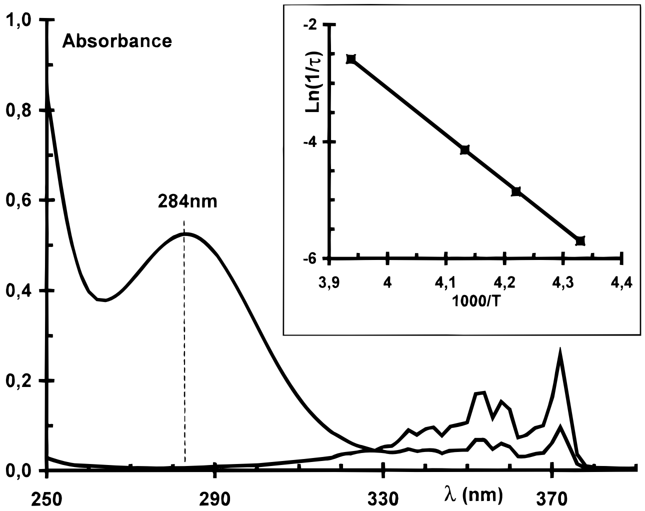


Figure 2. Absorption spectra of a solution of BCN diazirine in isooctane (20 mM, 1 mm optical path), before and after irradiation at −40 °C. Inset: Arrhenius plot for the decay of the species responsible of the absorption at 284 nm.

completely absent and a new absorption band, with a maximum at 284 nm, may be observed in the 260−320 nm region. Then, in a thermal process, this band slowly disappears while the azine absorption rises, whereas the absorption of the diazo remains unchanged. The study of the kinetic of decay of the absorption at 284 nm as a function of temperature (inset in Figure 2) gives the following kinetic parameters: $A = 3 \times 10^{12}$ s^{-1} and $E_a = 15.9$ kcal/mol. By analogy with the results previously obtained with the Ad:AdN2 system, the species responsible for the 284 nm absorption is assigned to the CDY ylide.

A large fraction of the diazirine must be photolyzed in order to get a satisfactory amplitude for the 284 nm absorption (about 50% on Figure 2), whereas for the Ad:AdN2 system in the same conditions, photolysis of only 1−3% of the diazirine gave a CDY absorption of a similar amplitude. Since the CDY ylides of these two systems should have similar absorption coefficients, the yield of formation of CDY must be much lower in the case of BCN:BCN(N_2), because either the rate constant of the reaction carbene + diazirine → CDY is much smaller or the lifetime of the carbene is much shorter. We estimated the lifetime of the BCN: carbene by using the pyridinium ylide technique, i.e., by measuring A_{385}, the amplitude of the absorption of the pyridinium ylide at 385 nm, as a function of the concentration of pyridine.

It has been shown[8] that the plots of $1/A_{385}$ vs 1/[pyridine] must be linear with a slope/intercept ratio $= k_1/k_{pyr}$, where k_1 is the reciprocal lifetime of the carbene in the absence of pyridine and k_{pyr} is the rate constant of the reaction carbene + pyridine → ylide. In isooctane (dried over molecular sieves, N_2 flushed, [diazirine] = 2.78 mM), the linear regression of $1/A_{385}$ vs 1/[pyridine] gives $k_1/k_{pyr} = 0.08 \pm 0.009$ (inset in Figure 3), whereas the nonlinear regression of the data A_{385} vs [pyridine], a preferable method,[9] gives $k_1/k_{pyr} = 0.094 \pm 0.009$ (see Figure 3). A similar experiment in aerated solution with [diazirine] = 6.67 mM gave $k_1/k_{pyr} = 0.107 \pm 0.015$ M^{-1}, indicating that the effects of [diazirine] and dissolved O_2 on the value of k_1 are within the error limits. With $k_1/k_{pyr} \approx 0.1$ and assuming that $k_{pyr} = 5 \times 10^9$ M^{-1} s^{-1} as for Ad:, the experiment yields a lifetime of BCN: around 2 ns, a value at least 100 times shorter than the lifetime of Ad:. Probably, BCN: as its N-methylated analogue, the *N*-methyl-3-azabicyclonon-9-ylidene,[10] suffers a rapid 1,3-CH insertion. This rearrangement is much faster than it is in the case of Ad:.

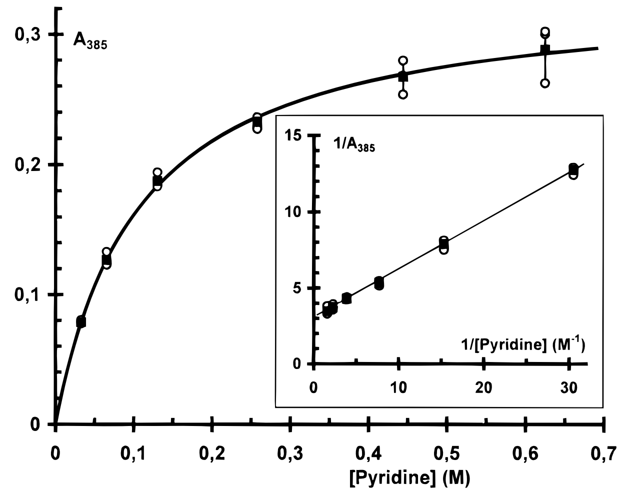


Figure 3. Amplitude of pyridinium ylide absorption at 385 nm, as a function of [pyridine]. The solid line is the nonlinear regression curve $A_{385} = ab[\text{pyridine}]/(1 + b[\text{pyridine}])$ with $a = 0.333$ and $b = k_{yl}\tau = 9.437$. Inset: Double reciprocal plot: $1/A_{385} = 1/a \times \{1 + 1/(b[\text{pyridine}])\}$.

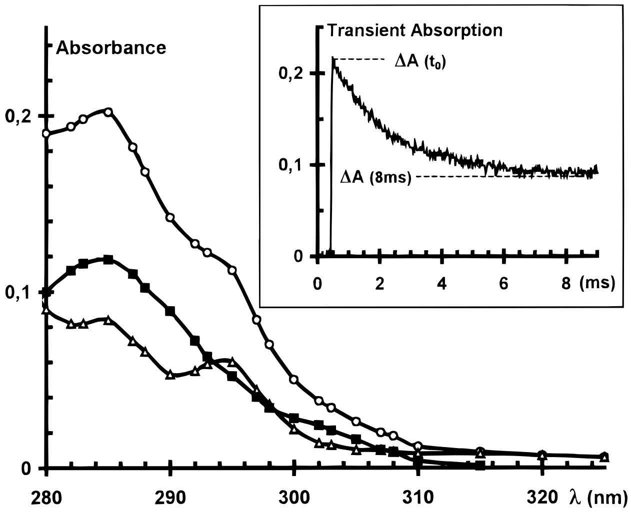


Figure 4. Benzylchlorocarbene in isooctane at −30 °C. Transient absorption spectra recorded 10 μs (O−O) and 8 ms (Δ−Δ) after excitation by a 200 ps laser pulse at 355 nm. Curve (♦−♦) is the differential spectrum ("10 μs" − "8 ms"). Inset: Trace of transient absorption vs time at 285 nm.

3.2. Benzylchlorodiazirine (BzClC(N_2)). We studied solutions of benzylchlorodiazirine in isooctane (≈12 mM, 10 mm cell) by laser flash photolysis (355 nm) at various temperatures, ranging from −2 to −50 °C. We recorded the changes in the values of the absorbance in the 280−330 nm region as a function of time over several milliseconds. Typical results obtained at −30 °C are presented in Figure 4. The "transient absorption spectrum" obtained 8 ms after excitation corresponds to the absorption spectrum of β-chlorostyrene, the stable product of 1,2-H shift rearrangement. The "transient absorption spectrum" measured 10 μs after excitation is more intense even if it shows a similar structure with bump or shoulder at 285 and 295 nm. It is clearly due to β-chlorostyrene, plus at least one other species which decays with a 1.8 ms lifetime at this temperature.

The absorption spectrum of the second species is obtained by the difference between the spectra recorded 10 μs and 8 ms after excitation. This spectrum consists of a broad structureless absorption band, with a maximum around 285 nm, similar to the absorption band measured for the CDY ylide in the Ad and

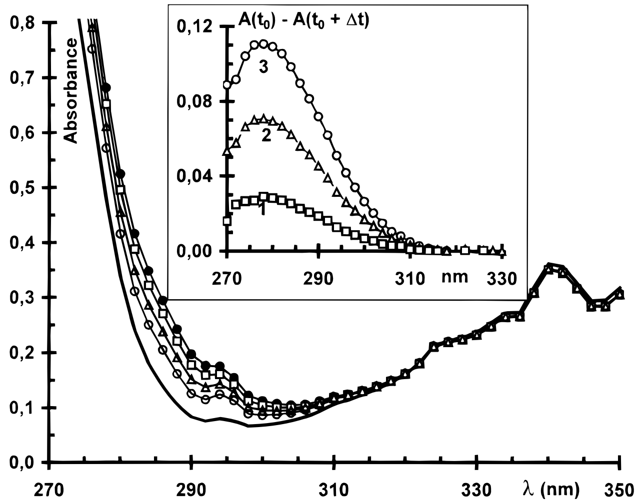


Figure 5. Benzylchlorodiazirine in isooctane at −95 °C. Absorption spectra before irradiation (full line), after irradiation (full circles), 30, 90, and 300 s later (open squares, triangles and circles). Inset: Differential spectra ("after irrad. " − "30, 90 or 300 s later".

BCN systems. An Arrhenius plot, log(1/τ) vs 1/T, where τ is the decay time of the absorption at 285 nm, gives an activation energy of $E_a = (11.5 \pm 0.4)$ kcal/mol and a frequency factor $A = 10^{12.9\pm0.4}$ s^{-1}. From these values of A and E_a, the lifetime of CDY should be several seconds at −95 °C, so that this species should be observable by conventional UV spectroscopy. We irradiated a concentrated solution of benzylchlorodiazirine in isooctane in a 1 mm cell at −95 °C by 10−20 laser pulses at 355 nm (10 Hz, 10 mJ/pulse), and the absorption spectrum was then recorded every 5 s during several minutes.

Four of these absorption spectra are shown in Figure 5, along with the absorption spectrum of the cold solution before irradiation. The differences between the spectrum recorded immediately after irradiation and those recorded 5, 15, and 60 s later are shown on the inset in Figure 5. In first approximation, they represent the absorption spectrum of a species disappearing[11] with a 13 s lifetime and identified as the CDY ylide because this lifetime's value fits the value expected from the kinetic parameters given above, and because the absorption spectrum resembles those presented in Figures 4 and 2.

3.3. Cyclopropylchlorodiazirine (cPrClC(N$_2$)). We irradiated fairly concentrated solutions of this diazirine in isooctane ($A_{355} = 0.8$/mm) by 50 laser pulses at 355 nm (10 Hz, 10 mJ/pulse) at −95 °C. We recorded the absorption spectrum immediately after the end of irradiation and then at regular time intervals. The results are shown in Figure 6 and the differential spectra "absorption after irradiation minus absorption after some delay" are shown on the inset of the same figure.

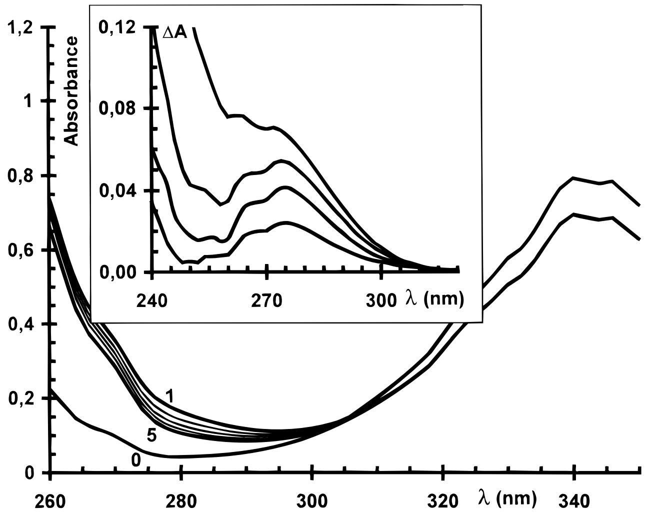


Figure 6. Cyclopropylchlorodiazirine in isooctane at −95 °C. Absorption spectra recorded before irradiation (0), immediately after irradiation (1) and 15, 45, 120, and 300 s later (2−5). Inset: Differential spectra (1 − 2), (1 − 3), (1 − 4), and (1 − 5).

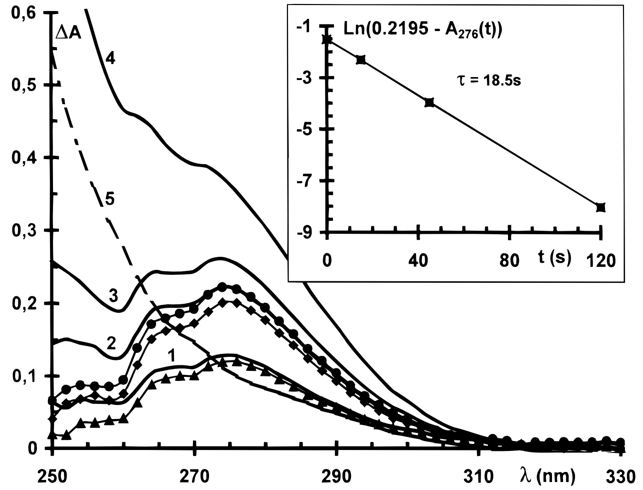


Figure 7. Cyclopropyldiazirine in isooctane at −95 °C. Curves 1−4 are the differential spectra shown on the inset of Figure 6. Curve 5 (dashed line) is the difference (curve 4 − curve 3) and corresponds to the tail of the absorption spectrum of the diazo. Curves with symbols are curves 1−3 corrected by the decay of the diazo during the corresponding period of time (8%, 19%, and 35% of curve 5, respectively). They represent the spectrum of the CDY ylide which decays with a 18.5 s lifetime obtained from the first-order kinetic analysis of the absorbance at 276 nm shown on the inset.

Two decaying species absorb radiation in the 250−310 nm region: the first one, with a lifetime estimated to be approximately 20−30 s and a maximum absorption of around 275 nm, is assumed to be the CDY ylide because its absorption spectrum resembles the spectrum of the CDY ylides obtained for other systems; the second has a longer decay time and an absorption predominance in the 250−270 nm range of wavelengths. The absorption spectrum of this second species is given by the difference between the spectra recorded 120 and 300 s after irradiation, since the concentration of the first species is negligible after 120 s (4−6 times the τ value). It is shown in Figure 7 (curve 5) and appears as the tail of an absorption spectrum with a maximum absorption well below 250 nm, which is probably to be assigned to the diazo compound. The differential spectra shown on the inset of Figure 6 have been reproduced in Figure 7 (curves 1−4): they represent the sum of the absorption of the species that disappeared during the 15, 45, 120, and 300 s after irradiation (i.e., CDY and the diazo) minus the absorption of the species formed during the same periods of time (i.e., the azine). Assuming that the absorption of the azine is negligible, curves 1, 2, and 3 have been corrected by the contribution of the diazo, estimated to be 8%, 20%, and 35% of the curve 5[12] to give the absorption spectrum of CDY at time t = 15, 45, and 120 s. A first-order analysis of the amplitude of this corrected absorption as a function of time (inset in Figure 7) yields a 18.5 s lifetime for CDY at −95 °C.

Laser flash photolysis of isooctane solutions ($A_{355} \approx 1$/cm) between −3 and −20 °C reveals the existence of a transient species absorbing in the 270−290 nm region, formed within less than a microsecond, decaying in the millisecond time scale and assigned to the CDY ylide on the basis of its absorption spectrum. The kinetic analysis of its decay at −8 °C yields a

0.5 ms lifetime but is inaccurate because the amplitude of this transient absorption is minute due to a low yield of formation of the CDY ylide. This low yield of formation indicates a low value of the rate constant of the reaction between the carbene and its parent diazirine, in agreement with previous observations,[3] from which it can be deduced that k_{az} is $<3 \times 10^6$ M^{-1} s^{-1}.

From the lifetimes measured at −95 (18.5 s) and at −8 °C by flash photolysis (0.5 ms), the following values for the kinetic parameters of the rearrangement CDY ⇒ azine emerge: E_a = 11.4 kcal/mol and $A = 10^{12.64}$ s^{-1}. These numbers are only approximate values because we did not accurately measure the lifetime values due to the small size of the transient, but they are close to those measured for the benzylchlorocarbene system.

3.4. Phenylchlorodiazirine (PhClC(N_2)). The lifetime of phenylchlorocarbene, PhClC:, is long in deaerated isooctane.[13] Azine is one of the major photoproducts, which clearly appears as a "permanent" absorption on the decay curves obtained at 300 nm in flash photolysis experiments. Attempts to observe the ylide by flash photolysis at room temperature and by conventional spectroscopy immediately after photolysis at −90 °C failed. The latter experiment suggests that the lifetime of the expected ylide is shorter than a few seconds at −90 °C. Assuming that the *A* factor for the conversion of the ylide into azine is still approximately 3×10^{12} s^{-1}, the E_a of this process is therefore less than 10 kcal/mol. Based on these values of *A* and E_a, the rate constant of the reaction ylide → azine must be larger than 10^5 s^{-1} at 20 °C, much bigger than the rate of the formation of the ylide, $\approx 5 \times 10^3$ s^{-1}, as estimated with [diazirine] ≈ 5 mM and $k_{yl} \approx 10^6$ M^{-1} s^{-1} (see note 12). This explains why the ylide is not observed by flash photolysis at room temperature.

4. Discussion

Concerning the decay of the CDY ylide, the activation energy for the reaction(s) responsible for this decay is lower for the two alkylchlorocarbenes studied ($E_a \approx 11.5$ kcal/mol) than for the two dialkylcarbenes ($E_a \approx 15.5$ kcal/mol). The Cl atom appears to stabilize the transition state between the ylide and the azine. For the PhClC: system, the value of E_a seems to be even smaller, less than 10 kcal/mol, probably related to the fact that the azine moiety is strongly stabilized by π conjugation with the two phenyl rings.

Concerning the formation of the CDY ylide, the rate constant of the carbene + diazirine reaction, k_{yl}, decreases when going from the dialkylcarbenes (3×10^9 M^{-1} s^{-1}) to benzylchlorocarbene (3×10^8 M^{-1} s^{-1}) and to phenylchlorocarbene (≈10^6 M^{-1} s^{-1}). It should be noticed that k_{yl} is at least 100 times smaller for cPrClC: than for BzClC. Recall that the rate constant of formation of the pyridinium ylide, k_{pyr}, is approximately 20 times smaller for cPrClC: than for several other alkylchlorocarbenes;[14] k_{pyr} being close to the diffusion control limit in the latter cases is what probably limits the range of variation of this rate constant. This seems to be correlated with a stabilization of this carbene by interaction of the carbene center with the "banana-shaped" orbitals of the cyclopropyl ring.

Does CDY yield exclusively azine, and what are the consequences of the formation of this ylide on previous studies? Some years ago, measurements of the lifetime of BzClC: as a function of temperature gave us nonlinear Arrhenius plots, the lifetime tending, at low temperatures, to a limit of around 100 ns due to reactions with an extremely low activation energy.[15] Recently, it was found that lowering the concentration of diazirine improves the linearity of the Arrhenius plot and that the yield of azine increases when the temperature decreases.[16] Clearly, the reaction between the carbene and the diazirine, a reaction with a very low E_a,[17] is one of the reactions responsible for the limit value of the carbene lifetime at a low temperature even if other reactions of the carbene (e.g., with the solvent and moisture or dimerization) certainly do also contribute since the plot of $\ln(1/\tau_{meas} - k_{yl}[\text{diazirine}])$ vs $1/T$ is still curved. The calculated yield of formation of CDY, $\Phi_{ylide} = k_r[\text{diazirine}]\,\tau_{meas}$, is 2.5 ± 0.5 times larger than the experimental yield of formation of azine as shown in Table 1.

TABLE 1: $\Phi_{azine}^{calc} = k_{yl}[\text{Diaz.}]/(k_{12} + 2.5 \times 10^6 + k_{yl}[\text{Diaz.}])^a$

temp (°C)	22	0	−35	−70
Φ_{azine}^{calc} (%)	4.96	10.60	37.35	84
Φ_{azine}^{meas} (%)	1.64	5.15	13.7	30.3
ratio	3.0	2.0	2.7	2.8

[a] [Diaz.] = 7 mM, $k_{12} = 10^{12} \exp(-6000/RT)$, and $k_{yl} = 3.5 \times 10^8$ M^{-1} s^{-1}. Φ_{azine}^{meas} from literature data (Table 1 in ref 15).

This difference, if not due to errors in the values of k_{yl} and τ_{meas}, means that CDY does not yield the azine quantatively. For instance, a 1,2 shift rearrangement could occur within CDY and yield chlorostyrene and diazirine. Such a hypothesis has been proposed already to explain the fact that photolysis of neat *p*-CF_3-benzylchlorodiazirine gives 50% azine and 40% chlorostyrenes, whereas, from the values of the rate constants k_{yl} and k_{12}, 98% of the carbene should react with the diazirine.[18] Similar results have been obtained by thermolysis of the diazirine indicating that the chlorostyrenes do not originate from rearrangement in an excited state (RIES pathway).[19] Also, a 1,2-H shift occurring within the 2-vinylpyridinium ylide of BzClC: has been proposed to explain the low yield of indolizine formed from this ylide whereas an indolizine is formed quantitatively from the 2-vinylpyridinium ylide of PhClC:.[20]

In Figure 4, the spectrum recorded 10 μs after excitation corresponds to remaining diazirine + chlorostyrene + CDY and the one recorded 8 ms later corresponds to remaining diazirine + chlorostyrenes + products formed from CDY. The difference is the spectrum of CDY minus the spectrum of the products formed from CDY. The absorption spectrum of azine is a broad band, without structure in the wavelength region of interest, whereas the absorption spectrum of chlorostyrene presents well-defined maxima at 295 and 285 nm. The quite smooth shape of the differential spectrum, which does not show any dip at 295 nm, seems to indicate that β-chlorostyrene is not formed from CDY. However, taking into account the values of the absorption coefficients, ≈$(3-5) \times 10^4$ M^{-1} cm^{-1} for CDY[21] and $<10^3$ M^{-1} cm^{-1} for the styrene, the presence of chlorostyrene from CDY with a 50% yield could not be detected on the UV spectra. Therefore no definite conclusion concerning the reality of a 1,2-H shift within CDY can be drawn from these differential spectra.

5. Conclusion

The existence of a carbene−diazirine ylide as intermediate on the way to azine seems to be a general phenomenon for carbenes with a singlet ground state. This species is characterized by an UV absorption spectrum in the region of 275−290 nm. Depending on the system considered, it may be difficult or even, in some cases, impossible to observe this species. Its yield of formation, $\Phi = k_{yl}[\text{diazirine}]\tau$, may be inconveniently small, either because the lifetime of the carbene is short, as in the case of BCN:, or because the value of k_{yl} is small, as in the case of cPrClC:. In some other instances, its rate of formation,

k_{yl}[diazirine], may be slower than its rearrangement rate to azine, if the activation energy for the latter process is not sufficiently large, as is probably the case for phenylchlorocarbene.

Although the main reaction pathway of CDY is the formation of azine, we suspect, but cannot prove from the reported spectroscopic results, that, in some cases at least, this ylide may also suffer some intramolecular rearrangement(s) such as 1,2-H migration yielding to its decomposition to diazirine + the olefinic product of rearrangement.

Azine is also formed by a bimolecular reaction between two diazo molecules. The efficiency of this pathway depends on the system being considered because the quantum yield of formation of the diazo greatly depends on the nature of the diazirine (e.g., it is much larger when formed from dialkyldiazirines than from alkylchlorodiazirines). It also depends on the experimental conditions (concentration, intensity of irradiation, temperature, ...), which determine the "stationary" concentration of diazo under continuous irradiation.

References and Notes

(1) *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press Inc.: Stamford, Connecticut, 1998; Vol. 2.

(2) Moss, R. A.; Ho, G.-J. *J. Am. Chem. Soc.* **1990**, *112*, 5642. Liu, M. T. H.; Chapman, R. G.; Bonneau, R. *J. Photochem. Photobiol., A: Chem.* **1992**, *63*, 115. Liu, M. T. H.; Bonneau, R. *J. Org. Chem.* **1992**, *57*, 2483. Bonneau, R.; Liu, M. T. H. *J. Photochem. Photobiol., A: Chem.* **1992**, *68*, 97.

(3) Bonneau, R.; Hellrung, B.; Liu, M. T. H.; Wirz, J. *J. Photochem. Photobiol., A: Chem.* **1998**, *116*, 9. Pezacki, J. P.; Warkentin, J.; Wood, P. D.; Lusztyk, J.; Yazawa, T.; Gudmundsdóttir, A. D.; Morgan, S.; Platz, M. S. *J. Photochem. Photobiol., A: Chem.* **1998**, *116*, 9.

(4) Shustov, G. V.; Liu, M. T. H.; Houk, K. N. *Can. J. Chem.* **1999**, *77*, 540.

(5) Moss, R. A.; Ho, G.-J.; Shen, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1990**, *112*, 1638.

(6) Note 16 in ref 5.

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

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

(9) Bonneau, R.; Wirz, J.; Zuberbühler, A. D. *Pure Appl. Chem.* **1997**, *69*, 979.

(10) Oida, S.; Ohki, E. *Chem. Pharm. Bull.* **1967**, *15*, 545; *Chem. Pharm. Bull.* **1968**, *16*, 654.

(11) Because the sign of the difference, this absorption seems to undergo an exponential growth, $\Delta A = \Delta A_{max}(1 - \exp[-(t/\tau)])$.

(12) These percentage values are obtained from the decay time of the diazo (~3.5 min at −95 °C) and then refined (by less than 10%) in order to get homothetic absorption spectra for CDY at the various delay times.

(13) "Lifetimes" around 3 μs are obtained by extrapolation to 0 of the plots $1/\tau$ vs [alkene] in the paper by: Turro, N. J.; Butcher, Jr., J. A.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576. In isooctane, PhClC: decays by a second-order reaction dimerization and pseudo-first-order reactions with solvent and diazirine ($k \approx 3 \times 10^3$ and 1.2×10^6 M^{-1} s^{-1}, respectively; Bonneau, R.; Grobys, M. Unpublished results).

(14) Bonneau, R.; Liu, M. T. H.; Rayez, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 5974. See also: Liu, M. T. H.; Bonneau, R. *J. Phys. Chem.* **1989**, *93*, 7300. Moss, R. A.; Ho, G.-J.; Shen, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1990**, *112*, 1638.

(15) Liu, M. T. H.; Bonneau, R.; Wierlacher, S.; Sander, W. *J. Photochem. Photobiol., A: Chem.* **1994**, *84*, 133.

(16) Merrer, D. C.; Moss, R. A.; Liu, M. T. H.; Banks, J. T.; Ingold, K. U. *J. Org. Chem.* **1998**, *63*, 3010.

(17) The value of k_{yl} measured at −90 °C for the BzClC: system, 3×10^8 M^{-1} s^{-1}, is nearly the same as the value measured at room temperature for phenoxymethylchlorocarbene, 3.5×10^8 M^{-1} s^{-1} (Liu, M. T. H.; Chateauneuf, J. E. *Res. Chem. Intermed.* **1994**, *20*, 195).

(18) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1992**, *114*, 3604.

(19) Doyle, M. P.; Devia, A. H.; Basset, K. E.; Terpstra, J. W.; Mahapatro, S. N. *J. Org. Chem.* **1987**, *52*, 1619.

(20) Liu, M. T. H.; Romashin, Y. N.; Bonneau, R. *Int. J. Chem. Kinet.* **1994**, *26*, 1179.

(21) Assuming that the value of ϵ_{max} for CDY is similar in the BzClC: and the Ad: systems. In the latter, during the slow decay of CDY at −40 °C, the decrease of absorbance at 284 nm ($-\epsilon^{Y}{}_{284}\Delta$[CDY]) is about twice as large as the increase of the absorbance at 214 nm ($\epsilon^{Az}{}_{214}\Delta$[azine] $-$ $\epsilon^{Y}{}_{214}\Delta$[CDY]) with $\epsilon^{Az}{}_{214} \approx 2.5 \times 10^4$ M^{-1} cm^{-1}. Therefore the value of ϵ_{max} for the Ad:Ad(N_2) ylide, $\epsilon^{Y}{}_{284}$, must be $\leq 5 \times 10^4$ M^{-1} cm^{-1}, e.g., 3×10^4 M^{-1} cm^{-1} if $\epsilon^{Y}{}_{214} \approx 10^4$ M^{-1} cm^{-1}.