(9s): mp 194–195 °C (acetone); IR (KBr) 1650 (CO), 1570 (C=C); ^{1}H NMR 2.06 (s, CH_3CO), 3.26 (s, NCH_3), 4.01 (s, NCH_3), 4.95 (dd, *J* = 7.7, 4.4, 5-H), 5.43 (d, *J* = 4.4, 4-H), 5.92 (d, *J* = 7.7, 6-H), 7.10–7.40 (m, 4 H, indole, 2-H), 7.75 (d, *J* = 8, 4′-H), 10.31 (s, CHO); ^{13}C NMR, Table II. Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.51. Found: C, 73.66; H, 6.18; N, 9.49. **5-Acetyl-2-(2-formyl-1-methyl-3-indolyl)-1-methyl-1,2-dihydropyridine (8s)**: ^{1}H NMR 2.21 (s, CH_3CO), 2.83 (s, NCH_3), 4.07 (s, NCH_3), 5.08 (br d, *J* = 9.5, 3-H), 6.15 (br s, 2-H), 6.60 (br d, *J* = 9.5, 4-H), 7.10–7.50 (m, 4 H, indole, 6-H), 7.79 (d, *J* = 8, 4′-H), 10.22 (s, CHO); ^{13}C NMR, Table II.

Acknowledgment. This work was supported by the DGICYT (PB88-0316), Spain, and by the "Acciones Integradas Hispano-Alemanas" program (36B-1990 and 18B-1991).

Concurrent Hydrogen Migration and Nitrogen Extrusion in the Excited States of Alkylchlorodiazirines

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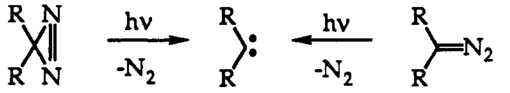
Received November 8, 1991

Laser flash photolysis of a series of alkylchlorodiazirines in the presence of pyridine generates easily detected, long-lived ylides. At large pyridine concentrations all of the alkylchlorocarbene generated in a laser flash is completely converted into ylide. The yield of ylide in this regime of pyridine concentration correlates with the α-C–H bond dissociation energy of the alkyl group. This demonstrates that hydrogen migration competes with carbene formation in the excited state of the precursor.

Introduction

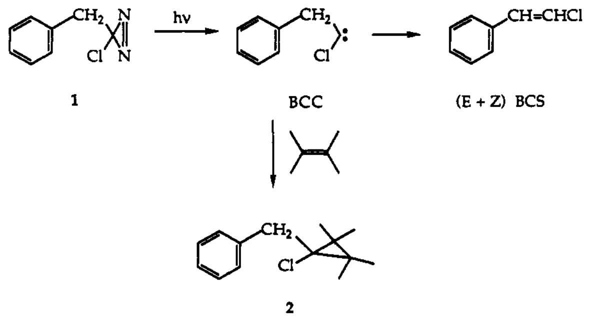
Carbenes have frequently been generated by the photochemical decomposition of diazirines and diazo compounds.[1] It has long been recognized that intramolecular



reactions of the excited states of the precursors may proceed in concert with nitrogen extrusion or that some rearrangement may occur in an excited state of the carbene.[2] In this circumstance the mixture of stable products formed on photolysis would reflect ground-state carbene reactions as well as the chemistry of the excited state of the precursor or the carbene. Identifying the origin (carbene or noncarbene) of a particular product or products is problematic at best.

A good example of these concerns is provided by benzylchlorocarbene BCC. Photolysis of benzylchlorodiazirine (**1**) in a relatively inert solvent produces a *Z* and *E* mixture of β-chlorostyrenes (BCS's), Scheme I.[3] Upon the addition of a carbene trap (e.g., tetramethylethylene) adducts **2** are formed. The presence of the trap has not only reduced the yield of BCS, but surprisingly the trap leads to a change in the *E*/*Z* ratio of the BCS rearrangement product. This result is inconsistent with the simple mechanism of Scheme I and requires that there are at least two pathways by which the chlorostyrenes are formed, a carbene and a noncarbene route. Liu has suggested that BCC forms a complex with alkenes[3] and that the complex can partition between cyclopropane formation and 1,2 hydrogen migration to form BCS with a new *E* + *Z* dis-

Scheme I



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(1) (a) Baron, W. J.; DeCamp, M. R.; Hendrick, M. L.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. I, p 1. (b) Nickon, A.; Huang, F.-chich; Weglein, R.; Matsuo, K.; Yagi, H. *J. Am. Chem. Soc.* **1974**, *96*, 5264. (c) Kyba, E. P.; Hudson, C. W. *J. Org. Chem.* **1977**, *42*, 1935. (d) Kyba, E. P.; Hudson, C. W. *J. Am. Chem. Soc.* **1976**, *98*, 5696. Kyba, E. P.; John, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 8329. (e) Press, L. S.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 509. (f) Seghers, L.; Shechter, H. *Tetrahedron Lett.* **1976**, *23*, 1943. (g) Freeman, P. K.; Hardy, T. A.; Baleat, J. R.; Wescott, L. D., Jr. *J. Org. Chem.* **1977**, *42*, 3356.

(2) (a) Chang, K. T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. (b) Gallucci, R. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 7704. (c) Kraska, A. R.; Chang, K. T.; Chang, S. J.; Moseley, C. G.; Shechter, H.; *Tetrahedron Lett.* **1982**, *23*, 1627. (d) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, *16*, 1733. (e) Kirmse, W.; Buschoff, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 692. (f) Frey, H. M.; Scaplehorn, N. *J. Chem. Soc. A* **1966**, 968.

(3) (a) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1990**, *112*, 3915. (b) Liu, M. T. H.; Murray, S. K.; Zhu, J. *Chem. Commun.* **1990**, 1650. (c) Stevens, I. D. R.; Liu, M. T. H.; Soundararajan, N.; Paike, N. *Tetrahedron Lett.* **1989**, *30*, 48. (d) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1989**, *111*, 6873. (e) Liu, M. T. H.; Subramanian, R. *J. Phys. Chem.* **1986**, *90*, 75 (benzyl bromo). (f) Liu, M. T. H.; Bonneau, R.; Rayez, M. *J. Am. Chem. Soc.* **1989**, *111*, 5973. (g) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1989**, *111*, 6873. (h) Tomioka, H.; Huyashi, N.; Izawa, Y. *J. Am. Chem. Soc.* **1984**, *106*, 454. (i) Bonneau, R.; Liu, M. T. H.; Subramanian, R.; Linkletter, B. *Laser Chem.* **1990**, *10*, 267. (j) Liu, M. T. H.; Subramanian, R. *J. Phys. Chem.* **1986**, *90*, 75. (k) Liu, M. T. H.; Bonneau, R. *J. Phys. Chem.* **1990**, *93*, 7298. (l) Stevens, I. D. R.; Liu, M. T. H.; Soundararajan, N.; Parke, N. *Tetrahedron Lett.* **1989**, *30*, 48.

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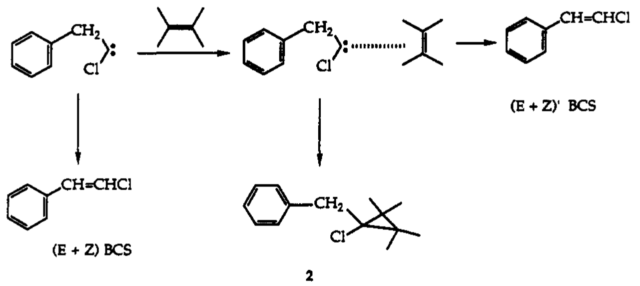
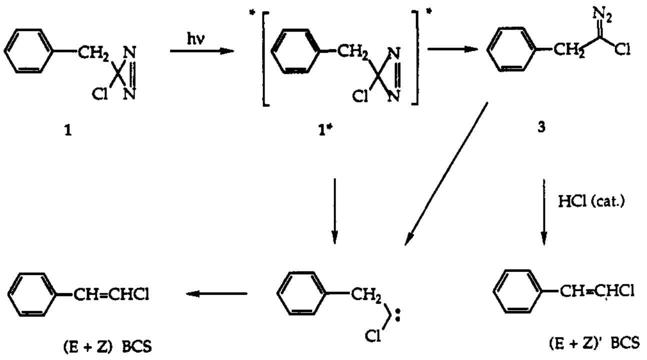
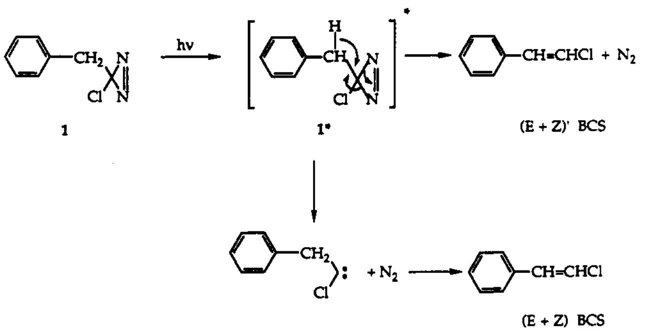
Scheme II



Scheme III

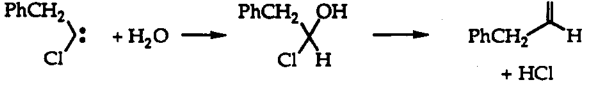


Scheme IV



tribution ($E + Z$)′ that is distinct from that of the carbene rearrangement (Scheme II).

Warner[4] has proposed that the second source of BCS is an excited state of the carbene BCC*. It is also possible that diazirine 1 isomerizes to diazo compound 3, which may then undergo acid-catalyzed decomposition to form β-chlorostyrenes with their own characteristic ($E + Z$)′ distribution (Scheme III). The acid catalyst (HCl) may be formed as a byproduct of the reaction of BCC with adventitious water, followed by hydrolysis of the geminal chlorohydrin product.



The diazirine 1 may also decompose to styrene by loss of nitrogen in concert with hydrogen migration (Scheme IV).

Herein we are pleased to report evidence that 1,2 hydrogen migration in the excited states of alkylchlorodiazirines is a general phenomenon (Scheme IV), and its importance is highly dependent upon the bond dissociation energy of the migrating hydrogen. We will also present spectroscopic evidence for the formation of diazo compound 3. This data, in combination with chemical trapping studies, demonstrates that the excited states of alkylchloro diazirines decay through at least three reaction pathways. These results eliminate the need to postulate carbene–alkene complexes formed in the reaction of BCC with alkenes.

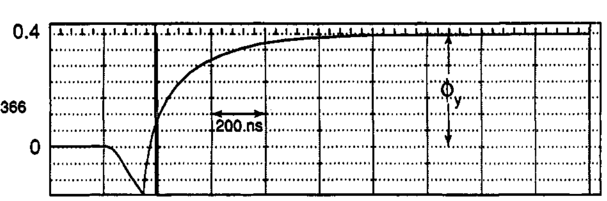


Figure 1. Formation of a pyridine ylide following laser flash photolysis of *tert*-butylchlorodiazirine (8) in CH_2Cl_2 at ambient temperature.

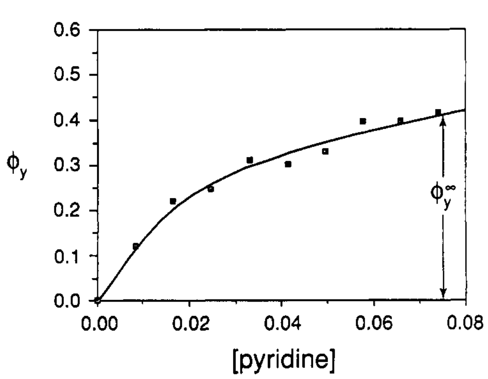
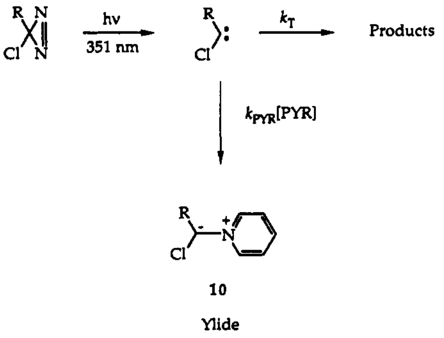


Figure 2. Yield of ylide (ϕ_y) as a function of [pyridine] upon photolysis of *tert*-butylchlorodiazirine.

Scheme V



Results

Laser Flash Photolysis Studies. Since their introduction in 1988 pyridine ylides[5] have become increasingly popular probes of the dynamics of carbenes which lack chromophores. In a typical experiment a diazirine is photochemically decomposed in the presence of pyridine, and the rate of formation of the ylide is recorded. A typical example of ylide formation is provided in Figure 1. The exponential growth of the ylide can be fit to an observed

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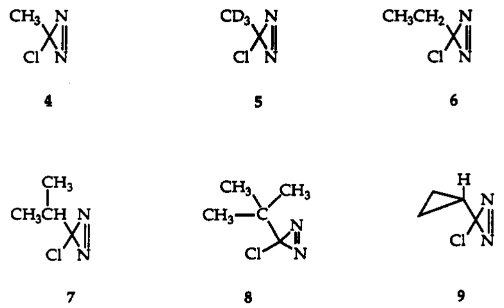
[4] Warner, P. M. *Tetrahedron Lett.* **1984**, *25*, 4211.

[5] (a) Zugravescu, I.; Petrovanu, M. *N-Yid Chemistry*; McGraw Hill: New York, 1976. (b) Jackson, J. E.; Platz, M. S. In *Advances in Chemical Applications of Lasers*; Brinker, U., Ed.; JAI Press: Greenwich, CT, in press. (c) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595. (d) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Doyle, M. P.; Liu, M. T. H.; *Tetrahedron Lett.* **1989**, *30*, 1335. (e) Jackson, J. E.; Soundararajan, N.; White, W.; Liu, M. T. H.; Bonneau, R.; Platz, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 6874. (f) Ho, G. J.; Krogh-Jespersen, K.; Moss, R. A.; Shen, S.; Sheridan, R. S.; Subramanian, R. *J. Am. Chem. Soc.* **1989**, *111*, 6875. (g) Chateauneuf, J. E.; Johnson, R. P.; Kirchoff, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 3217. (h) White, W.; Platz, M. S.; Chen, N.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 7794.

Chart I



rate constant k_{obs} which is related to the kinetics of Scheme V as given in eq 1,[6] where k_{PYR} is the absolute rate constant

$$k_{obs} = k_T + k_{PYR}[PYR] \qquad (1)$$

of reaction of an alkylchlorocarbene with pyridine and k_T is the total of all first-order and pseudo-first-order processes which consume the carbene in the absence of pyridine. A typical plot of the yield of ylide, ϕ_y, versus pyridine is given in Figure 2. Obviously $\phi_y = 0$ when [pyridine] = 0 and increases steadily as [pyridine] increases. Typically, when [pyridine] > 0.5 M, the yield of ylide is saturated. In this pyridine concentration regime all of the alkylchlorocarbene generated in a single laser pulse is converted to ylide. The diazirines of Chart I were synthesized, and all produced the transient spectrum of an ylide upon LFP in the presence of pyridine in methylene chloride.

There is tremendous variation in the yield of ylide at saturation with diazirine, ϕ^{∞}, upon LFP of solutions of alkylchlorodiazirines with equal optical densities (A_{351} = 0.363–0.370). The signals obtained from **8** and **9** (Chart I) are more than 10 times as large as those obtained from isopropylchlorodiazirine (**7**). *tert*-Butylchlorodiazirine (**8**), which lacks an α-C–H bond, behaves in a manner very similar to that of cyclopropylchlorodiazirine **9** and generates a very intense ylide signal at saturation. The optical yield of ylide at saturation should mirror the relative yield of ylide as a function of diazirine precursor, as we expect that the molar absorptivities (extinction coefficients) of ylides **10** (Scheme V) are independent of the nature of the alkyl group. Thus, the optical yield of ylide at saturation tracks the yield of carbene produced in a laser pulse, for a given diazirine. The variation in the yield of ylide reflects the efficiency with which a given diazirine excited state decomposes to form a carbene. As demonstrated in Figure 3 the yield of carbene at saturation correlates closely with the bond dissociation energy[7] of the C–H bond positioned α to the diazirine carbon, assuming that the diazirine moiety has the same effect on adjacent CH bonds as a methyl substituent.

The yield of ylide from trideuteriomethylchlorodiazirine (**5**) is 9% larger than the yield of ylide obtained from methylchlorodiazirine (**4**). This is consistent with the lower zero-point energy of a C–D bond and the greater strength of a C–D bond relative to a C–H bond.[7] Furthermore, our assumption that the extinction coefficients are independent of the nature of the alkyl CH bond is probably most valid in the comparison of diazirines **4** and **5**.

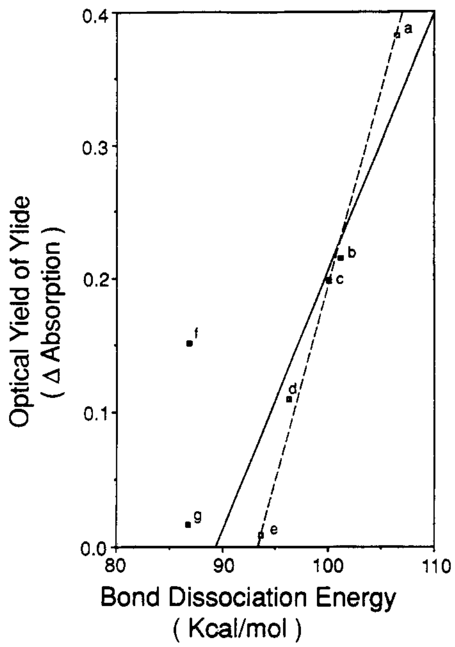


Figure 3. Yield of ylide (ϕ_y) as a function of bond dissociation energy of the α-CH bond, broken line excluding BCC ylide, solid line including BCC-ylide, corrected; the ylides were derived from diazirines (a) **9**, (b) **5**, (c) **4**, (d) **6**, (e) **7**, (f) **1**, not normalized, and (g) **1**, normalized.

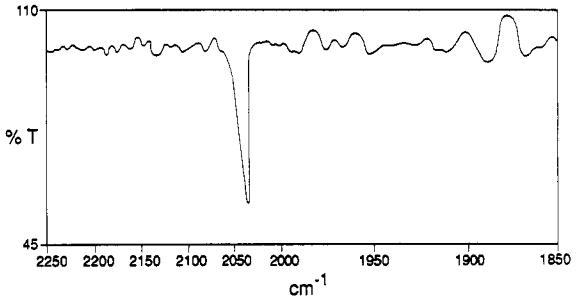


Figure 4. Diazo stretch of benzylchlorodiazomethane (**3**) in glassy 3-methylpentane at −175 °C.

A simple interpretation of this data is that an α-hydrogen of the alkylchlorodiazirine excited state undergoes 1,2 hydrogen migration concurrent with nitrogen extrusion (Scheme IV). Some alkene product is thereby formed directly from the excited state of the diazirine, bypassing the carbene intermediate. It is certainly likely that the E/Z ratio of alkene product formed from the diazirine excited state will differ from the E/Z ratio of alkene formed from the carbene.

The yield of carbene is large with *tert*-butylchlorodiazirine (**8**) and cyclopropylchlorodiazirine (**9**) because the α-C–H bond is either very strong or nonexistent. Apparently, α-carbon does not migrate as efficiently as hydrogen in the excited states of simple alkylchlorodiazirines. Similar conclusions were reached by Çelebi[8] in a study of arylalkyldiazomethanes. In separate studies Goodman[9a] and Morgan[9b] have also provided evidence that diazirine excited states undergo more chemistry than simple extrusion of nitrogen and carbene formation. Çelebi[8] and Morgan[9b] have also demonstrated that diazirine and diazo excited states do not react with pyridine to form ylides.

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(6) The pyridine probe method is based upon models developed by Scaiano to probe free-radical reactions. For examples, see: (a) Small, R. D., Jr.; Scaiano, J. C. *Phys. Chem.* **1977**, *81*, 828. (b) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431. (c) *Ibid.* **1978**, *59*, 246.

(7) (a) Kerr, J. A.; *Chem. Rev.* **1966**, *66*, 465. (b) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. (c) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 492.

(8) Çelebi, S.; Platz, M. S. *J. Am. Chem. Soc.*, submitted for publication.

(9) (a) LaVilla, J. A.; Goodman, J. *Tetrahedron Lett.* **1990**, *31*, 5109. (b) Morgan, S.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2782.

Table I. E/Z Ratio of β-Chlorostyrenes Formed as a Function of Solvent Produced by Extended Photolysis of 1 and Reported Absolute Rate Constants

solvent (neat trap)	E/Z	$k_Q{}^b$ (M^{-1} s^{-1}) 25 °C[3]
tetramethylethylene	1.02	1.1×10^8
CH_3OD	0.75	9.4×10^8
pyridine	1.56	4.2×10^9
CH_2Cl_2	1.75	*b*
1,2 hydrogen migration		$4.9–6.7 \times 10^{7\,c}$

[a] Absolute rate constant for solvent quencher, Q. [b] CH_2Cl_2 does not react with BCC. [c] First-order rate constant in units of s^{-1}.

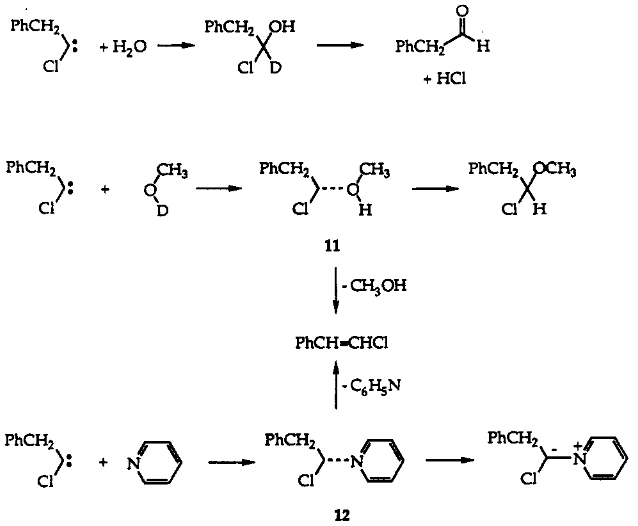
In the case of the BCC pyridinium ylide the optical density of the ylide at saturation is much greater than would be expected based on the α–C–H bond strength alone. However, the n–π^* electronic transition of the ylide may be significantly effected by α-phenyl substitution. We have chosen to model this effect by comparing the extinction coefficients of the n–π^* transitions of acetone and phenylacetone. The n–π^* transition of acetone (λ_{max} = 279 nm) has a molar extinction coefficient of 13 in several solvents.[10] The n–π^* transition (285.4 nm) of phenylacetone in CH_2Cl_2 was found to have an extinction coefficient of approximately 114 (λ = 285.4 nm). Accordingly, the optical density of the BCC pyridinium ylide was multiplied by the ratio of the extinction coefficients for the n–π^* transitions in acetone and phenyl acetone (0.114). This normalized value also appears in Figure 3 as the entry for BCC. This normalization factor brings the BCC result in line with the data of the simple alkylchlorocarbenes. It is interesting to note that the α-phenyl substituent red shifts the n–π^* transition of acetone and ylide 10 by roughly the same energy (2.3 and 2.6 kcal/mol, respectively).

If this correction of ylide absorption is *invalid* then Figure 1 predicts that the yield of carbene from benzylchlorodiazirine is only 40% of the yield of carbene obtained from cyclopropylchloro and *tert*-butylchlorocarbene. This is actually consistent qualitatively, but not quantitatively (vide infra), with the known photochemistry of benzylchlorodiazirine[3] (vide infra).

Chemical Analysis of Reaction Mixtures. Samples of diazirine 1 were prepared in methanol-OD, tetramethylethylene, pyridine, and in a more inert solvent, methylene chloride. Each sample tube was photolyzed until the diazirine precursor was completely consumed. Carbene adducts with the solvent trap were the principal products formed in methanol-OD and tetramethylethylene (TME) but significant yields of the beta chlorostyrenes were detected in every solvent. The E/Z ratios of the beta chlorostyrenes as a function of solvent are given in Table I.

The absolute rate constants of reaction of BCC with TME, CH_3OD, and pyridine are known,[3] as is the rate constant for 1,2 hydrogen migration in the carbene to form the β-chlorostyrenes.[3] Inspection of these rate constants (Table I) predicts that no BCS should be formed in neat TME, CH_3OD, or pyridine. The fact that styrenes are formed in these solvents further demonstrates that Scheme I is incomplete and that there must be a noncarbene pathway leading to the rearrangement product.

As mentioned previously, Liu and Bonneau[3] have associated the second styrene source as a carbene–alkene complex (Scheme II). These types of complexes were first proposed by Moss and Turro.[11] However, if this viewpoint is correct one must then require that BCC forms a complex with CH_3OD and with pyridine and that putative complexes 11 and 12 must also suffer 1,2 hydrogen migration in competition with the formation of ether and ylide, respectively. Although we cannot rule out that BCC forms a complex with several types of traps, the data requires additional assumptions to be made to prop up the carbene–alkene complex hypothesis.



Upon photolysis of benzylchlorodiazirine in neat alkene[3h] both cyclopropane adducts and alkenes are formed. The carbene–alkene complex hypothesis (Scheme II) interprets the ratio of cyclopropane/alkene product as the partitioning of a common intermediate, the complex. The excited-state hydrogen shift hypothesis (Scheme IV) associates the product ratio with the ratio of carbene formation to hydrogen migration in the excited state of the diazirine. Upon analysis of published chemical trapping data[3h] we deduce that benzylchlorodiazirine fragments to carbene with 80–85% efficiency and undergoes hydrogen migration with 15–20% efficiency per mole of diazirine decomposition. An efficiency of 80–85% is not in quantitative agreement with the predictions of Figure 1. This demonstrates that the extinction coefficient of the benzylchlorocarbene pyridine ylide is not the same as that of the simple alkylchloropyridine ylides.

In principle, one can distinguish the mechanisms of Schemes II and IV by plotting the yield of alkene/cyclopropane versus 1/[alkene]. Scheme IV predicts that these plots will have a common intercept that is independent of the nature of the alkene. Scheme II predicts variation of the intercept with the nature of the alkene. Three alkenes[3a] (*n*-butyl vinyl ether, chloroacrylonitrile, and TME) all have intercepts of ≈0.5 in these plots, diethylfumarate has an intercept of 2, and diethylmesaconate has an intercept of 3. In our opinion these data do not decisively distinguish Schemes II and IV.

Low-Temperature IR Spectroscopy. The isomerization of diazirines to diazo compounds is well documented.[12] To determine whether diazirine 1 isomerizes to diazo compound 3 the photochemistry of 1 was studied at low temperature. Photolysis (λ > 350 nm) of 1 in glassy 3-methylpentane at −175 °C leads to the formation of a new IR band at 2040 cm^{-1} which is readily attributed to 3.

The 2040 cm^{-1} band increases in intensity upon further photolysis at low temperature. Allowing the matrix to

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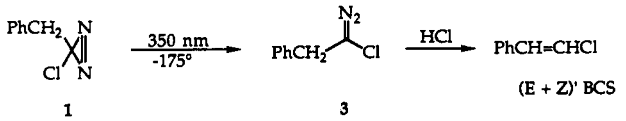
(10) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. In *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991; p 300.

(11) Moss, R. A.; Turro, N. J. In *Kinetics and Spectroscopy of Carbenes and Biradicals*, Platz, M. S., Ed.; Plenum: New York, 1990, p 213.



stand at −175 °C for several hours led to no appreciable decrease in the intensity of the diazo band. However, upon warming the sample to approximately −70 °C and refreezing, the diazo band was found to markedly decrease in intensity.

These results do not prove that 1 will also photoisomerize to 3 at ambient temperature; however, the low-temperature results are at the very least suggestive of this possibility. Thus, the diazo intermediate 3 is a plausible candidate for the requisite second route to BCS in the photolysis of alkylchlorodiazirines, as ionic decomposition of 3 need not form BCS product with the same *E*/*Z* ratio as benzylchlorocarbene.

Discussion

It is clear that the β-chlorostyrenes are photochemically formed from diazirine 1 by at least two pathways. Benzylchlorocarbene is an obvious candidate for one route to the olefinic product.

We have demonstrated that the yield of carbene produced from a given dizirine in a laser pulse is a function of the bond dissociation energy of the α-carbon–hydrogen bond. The excited state of the alkylchlorodiazirine can, in principle, fluoresce, intersystem cross to an excited triplet state, undergo internal conversion to the ground state, or suffer photochemical reactions.

No fluorescence was observed from benzylchlorodiazirine 1 at room temperature, nor was any fluorescence observed from 1 in glassy 3-methylpentane at −196 °C. Two known reactions of diazirines are the extrusion of nitrogen and carbene formation and isomerization to diazo compounds.[12] Both of these reactions are demonstrated for benzylchlorodiazirine 1. Carbene formation is demonstrated by the formation of adducts, direct detection by time-resolved UV–vis spectroscopy, and by pyridine ylide formation.[3] Diazo formation was demonstrated by detection of 3 by low-temperature IR spectroscopy. Unfortunately, there are no good models available for the extinction coefficients of the alkylchlorodiazo compound 3 or of chlorinated pyridine ylides such as 10; thus, we can not quantify the yields of these processes.

Figure 3 shows a strong dependence on the yield of carbene, per diazirine, per laser pulse on the strength of an adjacent CH bond. The large difference in carbene yield between isopropylchlorodiazirine (7) and cyclopropylchlorodiazirine (9) with its very strong α-C–H bond is particularly striking. We do not see how the α-C–H bond strength could dramatically influence the rate of intersystem crossing or the rate of internal conversion of the excited singlet state of the diazirine. We feel that a reasonable interpretation of the data is that an α-C–H bond can migrate in the excited state of the diazirine and form alkene in concert with nitrogen extrusion (Scheme III). This interpretation is strongly supported by the observation that deuterated diazirine 5 gives a higher yield of ylide (and carbene) than methylchlorodiazirine. If there is no rearrangement in the excited state of cyclopropylchlorodiazirine then we calculate that the efficiency of 1,2 hydrogen rearrangement in the excited states of methylchloro, methyl-d_3-chloro, ethylchloro, and isopropylchloro diazirine is 48.2, 43.7, 71.5, and 96.6%, respectively, per diazirine decomposition. There is no evidence for carbon migration in the excited states of alkylchlorodiazirines, and if this process occurs it is less efficient than hydrogen migration in simple alkylchlorodiazirines.

Our data are also consistent with hydrogen migration in an excited state of benzylchlorocarbene.[2,4] We prefer the diazirine excited state interpretation only for reasons of economy. An excited state of benzylchlorodiazirine is necessarily formed on photolysis of 1, and this state isomerizes to 3. There is no evidence to require us to postulate the presence of another reactive species such as BCC.*

Conclusion

The chemical trapping data require that the β-chlorostyrenes are formed by at least two pathways. In this work we have identified three distinct pathways by which alkylchlorodiazirines in general, and benzylchlorocarbene in particular, undergo decomposition; carbene formation, isomerization to alkylchlorodiazo compounds, and hydrogen migration and alkene formation in concert with nitrogen extrusion. The data do not eliminate the possibility of a carbene–alkene complex which can undergo 1,2 hydrogen migration in competition with cyclopropane formation but the data do not *require* the postulation of a benzylchlorocarbene–alkene complex. In our opinion there is at present no compelling reason to invoke the intervention of a carbene–alkene complex in the chemistry of benzylchlorocarbene.

Experimental Section

Materials. All of the alkylchlorodiazirines of this work are known compounds[13] and were prepared by literature methods. Methylene chloride was distilled from 4-Å molecular sieves (Aldrich) and stored over the same. Pyridine was distilled from barium oxide and stored over KOH pellets. Methanol-D was purchased from Aldrich and used as received. TME was distilled from 4-Å molecular sieves (Aldrich) and stored over the same. TME was passed through a short column of neutral alumina immediately prior to use. 3-Methylpentane was washed with concd H_2SO_4 until no further discoloration was observed, washed w/40% KOH in water, and distilled from and stored over KOH pellets. Methanol was distilled from sodium methoxide.

Laser Flash Photolysis. The LFP system in use at Ohio State has been described previously.[14] Solutions of the gaseous diazirines were prepared in previously distilled methylene chloride. The concentrations of diazirine were adjusted to closely match the absorbance of each solution at 351 nm. The actual absorbance values range from 0.363 to 0.370. To each 1.5-mL sample was added 250 μL of pyridine resulting in [PYR] = 1.77 M, well above the saturation point. Three transient spectra were recorded at λ_{max} for each ylide; the averages of three ylide yield readings are used in Figure 3.

Chemical Analysis of Mixtures Formed on Extended Photolysis of Diazirines. 3.0×10^{-1} M solutions of benzylchlorodiazirine (1) were prepared in methanol-OD, pyridine, methylene chloride, and tetramethylethylene (TME). After degassing and sealing the samples in Pyrex tubes, each was photolyzed in a Rayonet photoreactor fitted with four 350-nm bulbs. The samples were irradiated for 16 h and analyzed by capillary GC. In each case significant amounts of (*Z*)- and (*E*)-β-chlorostyrenes were produced. Photolysis of 1 in methanol-OD produces the β-chlorostyrene (BCC's) in an *E*/*Z* ratio of 0.75. In TME, pyridine, and methylene chloride the ratio is inverted and varies from 1.02 in TME to 1.56 in pyridine and 1.75 in CH_2Cl_2. The major product formed in the photolysis of 1 in TME or methanol-OD is the corresponding adduct.[3] In methylene chloride only

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(12) Meier, H. In *Chemistry of Diazirines*; Liu, M. T. H.; Ed.; CRC Press: Boca Raton, FL, 1987, Vol. II, p 1.

(13) Schmitz, E. In *Chemistry in Diazirines*; Liu, M. T. H., Ed.; CRC Press: Boca Raton, FL, 1987; Vol. 1, p 57.

(14) Soundararajan, N.; Platz, M. S.; Jackson, J. E.; Doyle, M. P.; Oon, S.-M.; Liu, M. T. H.; Anand, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 7143.

the two chlorostyrene products are formed. The photolysis of 1 in pyridine produces a black solution and a tarlike precipitate after only a few hours of photolysis. In each case TLC of the photolyzed mixtures demonstrates that there is no significant amount of unreacted diazirine present. ^{1}H NMR spectroscopy of the diazirine prior to photolysis demonstrates the absence of the chlorostyrenes in the starting material.

Low-Temperature IR Spectroscopy. A 2.4 M solution of benzylchlorodiazirine was prepared in 3-methylpentane. The solution was loaded into a CaF$_2$ low-temperature IR sample cell with a path length of 1 mm and cooled to -175 °C in an Aries low-temperature cell holder. Upon cooling, the solution formed a transparent glass. In the IR spectrophotometer (Perkin-Elmer 1710 FTIR) a background spectrum of the solution prior to photolysis was recorded and saved. The glass was photolyzed with a 150-W Xe arc lamp fitted with a 350-nm filter for varying time intervals. After photolysis, the infrared spectrum exhibits a particularly strong new absorption band centered at approximately 2040 cm^{-1}.

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Registry No. 1, 88211-05-6; 3, 71706-88-2; 3 carbene, 88211-07-8; 4, 4222-21-3; 4 ylide, 122567-46-8; 4 carbene, 31304-51-5; 5, 35496-73-2; 5 ylide, 139759-66-3; 5 carbene, 139759-68-5; 6, 29667-77-4; 6 ylide, 139759-67-4; 6 carbene, 69096-58-8; 7, 29648-80-4; 7 ylide, 139759-69-6; 7 carbene, 69096-59-9; 9, 4222-24-6; 9 ylide, 123027-57-6; 9 carbene, 68735-14-8; H$_3$COD, 1455-13-6; TME, 563-79-1; *E*-BCS, 4110-77-4; *Z*-BCS, 4604-28-8; pyridine, 110-86-1.

Photochemistry of Polyhaloarenes. 12. The Photochemistry of Pentachlorobenzene in Micellar Media[1]

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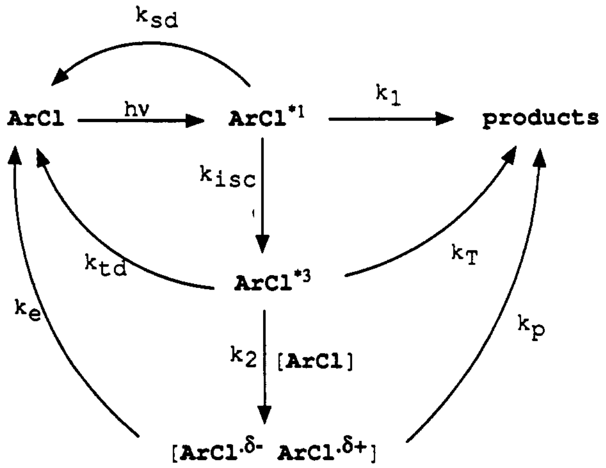
The dependence of the reciprocal of the quantum yield for the photohydrodechlorination of pentachlorobenzene (1) in aqueous 0.100 M hexadecyltrimethylammonium bromide (CTAB) solution upon the reciprocal of the microconcentration of 1 and upon the reciprocal of the probability for excited state 1 reacting with ground-state 1 provides a linear correlation at high microconcentrations of 1. The regiochemistry of the photohydrodechlorination process in CTAB favors formation of 1,2,4,5-tetrachlorobenzene to a significantly smaller extent than is observed in the analogous process in acetonitrile solution in the presence of triethylamine. The bromotetrachlorobenzene byproduct is formed in the photolysis in the following average composition: 1-bromo-2,3,4,5-tetrachloro- (5): 2-bromo-1,3,4,5-tetrachloro- (6): 3-bromo-1,2,4,5-tetrachlorobenzene (7) = 9.7:66.7:23.3. In a trapping experiment carried out during an irradiation of 1 in CH$_3$CN/H$_2$O (8:2) in the presence of excess KBr at 254 nm, bromotetrachlorobenzenes (5:6:7) were formed in a ratio of 11.3:66.8:21.9. These experiments are rationalized by proposing that product in these micellar photohydrodechlorination reactions is formed by fission of triplet-state 1 and a competing process which involves conversion of triplet-state 1 to triplet excimer which then undergoes fragmentation.

In recent studies carried out in this laboratory on the photochemistry of polyhaloarenes, attention has been focused on the mechanisms of phototransformations in homogeneous organic solvents,[2] with the exception of an investigation where micellar media were used to separate the radical cation near the micellar surface (Stern layer) from the radical anion in the interior; the radical cation and anion resulting from electron transfer from the electron donor on the surface to the polyhaloarene in the interior.[3] It appeared to us that additional efforts devoted to elucidation of the mechanisms of phototransformation of polyhaloarenes in micellar media were of considerable interest, since photodecomposition in the environment may occur in a micellar environment and since micellar media appear to offer considerable potential in the design of toxic waste disposal systems.

Scheme I



Photolysis of pentachlorobenzene (1) in acetonitrile at 254 nm at low conversions generates the three tetrachlorobenzene isomers (2, 3, and 4). Our recent analysis of the intersystem crossing yield and the quantum yield dependence upon substrate concentration, concentration of sensitizer and quencher, and intensity of light is consistent with three pathways to product: fission of singlet (k_1), fission of triplet (k_T), and fragmentation via the triplet excimer (k_p) (Scheme I). The major pathways to product

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[1] For paper 11 in this series see: Freeman, P. K.; Clapp, G. E.; Stevenson, B. K. *Tetrahedron Lett.* **1991**, 5705-5708.

[2] (a) Freeman, P. K.; Jang, J.-S.; Ramnath, N. *J. Org. Chem.*, in press. (b) Freeman, P. K.; Ramnath, N.; Richardson, A. D. *J. Org. Chem.* **1991**, *56*, 3643-3646. (c) Freeman, P. K.; Ramnath, N. *J. Org. Chem.* **1988**, *53*, 148-152. (d) Freeman, P. K.; Srinivasa, R. *J. Org. Chem.* **1987**, *52*, 252-256. (e) Freeman, P. K.; Srinivasa, R. *J. Org. Chem.* **1986**, *51*, 3939-3942. (f) Freeman, P. K.; Srinivasa, R.; Campbell, J.-A.; Deinzer, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 5531-5536. Freeman, P. K.; Srinivasa, R. *J. Agric. Food Chem.* **1984**, *32*, 1313. Freeman, P. K.; Jonas, V. *J. Agric. Food. Chem.* **1984**, *32*, 1307. Freeman, P. K.; Srinivasa, R. *J. Agric. Food Chem.* **1983**, *31*, 775.

[3] Freeman, P. K.; Ramnath, N. *J. Org. Chem.* **1991**, *56*, 3646-3651.

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