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Generation and Study of Benzylchlorocarbene from a Phenanthrene Precursor

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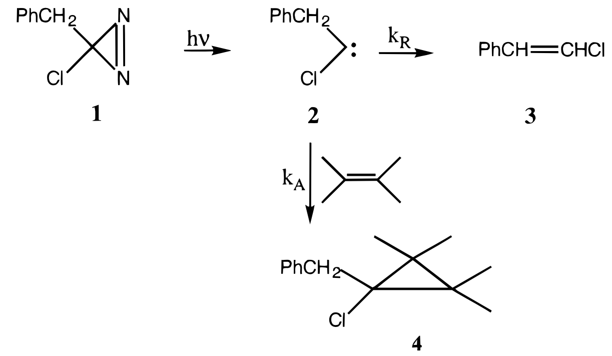
Abstract: The curved plots of (carbene adduct)/(carbene-rearrangement product) versus carbene trapping agent, tetramethylene [TME], reported with benzylchlorodiazirine **1** have been reproduced. However, with the use of a non-nitrogenous precursor, plots of this type are approximately linear over the range of [TME] employed. Thus, any complex formed between benzylchlorocarbene and TME must collapse to form cyclopropane faster then it can fragment with rearrangement to β-chlorostyrene and TME. Diazirine **1** does photoisomerize to diazo compound **7**, but this process is inefficient ($\phi = 0.075$) and is not likely to be responsible for the curvature in plots of adduct/styrene versus [TME] observed with the diazirine precursor. Thus, the second, noncarbene, pathway to β-chlorostyrene is neither a carbene−olefin complex nor a diazo intermediate. It is proposed that the second pathway involves a rearrangement in the excited state of the diazirine, although other explanations cannot be discarded.

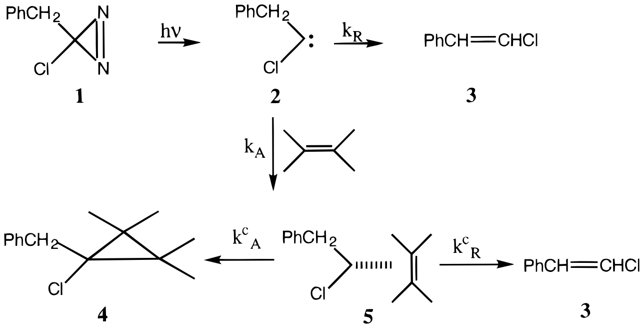
I. Introduction

In 1984 Tomioka, Liu, and co-workers reported that photolysis of benzylchlorodiazirine **1** produced benzylchlorocarbene **2** which rearranged to a mixture of *E* and *Z* β-chlorostyrenes **3**.[1] When the photolysis was repeated in the presence of tetramethylethylene (TME) cycloadduct **4** was isolated. A simple interpretation of the data (Scheme 1) predicts that a plot of **4**/**3** versus [TME] will be linear with a slope of k_A/k_R. The expected linear dependence was not observed, however. The data indicate that there are two pathways which form β-chlorostyrene product. It was proposed that carbene **2** reacts with TME to form a π complex (**5**) which partitions between collapse to form cyclopropane **4** ($k^c{}_a$) and rearrangement ($k^c{}_R$) to β-chlorostyrene **3**. Thus, not all of the carbene can be diverted to cyclopropane, even at infinite concentration of TME (Scheme 2). Furthermore, some dependence of the intercept of plots of [**3**/adduct (e.g., **4**)] versus 1/[alkene] on the nature of the alkene was found, as predicted by the carbene−alkene complex mechanism.[2] Subsequently, it was found that the *E*/*Z* ratio of β-chlorostyrenes varies with [TME], which is also consistent with Scheme 2. The kinetics and spectroscopy of benzylchlorocarbene have also been studied by laser flash photolysis techniques.[2,3]

Scheme 1



Scheme 2



Many groups have postulated that carbene−olefin complexes[4] (COC) are formed prior to the formation of cyclopropane.

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[§] University of New Hampshire.

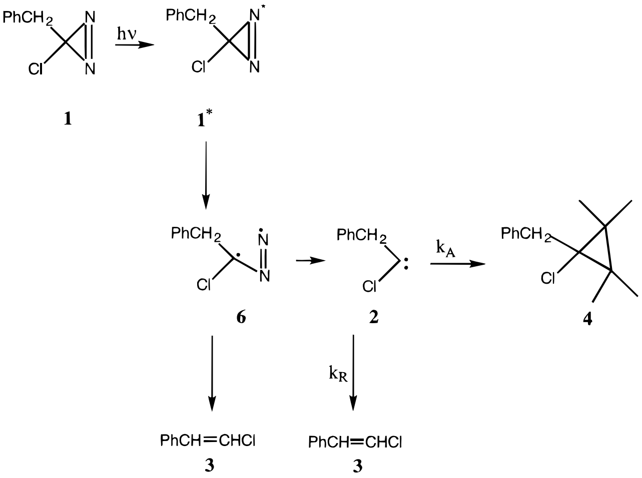
(1) Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Am. Chem. Soc.* **1984**, *106*, 454.

(2) (a) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1990**, *112*, 3915. (b) Liu, M. T. H.; Soundararajan, N.; Paike, N.; Subramaniam, R. *J. Org. Chem.* **1987**, *52*, 4223. (c) Liu, M. T. H.; Bonneau, R.; Wierlacher, S.; Sander, W. *J. Photochem. Photobiol. A: Chem*. **1994**, *84*, 133. (d) New Arrhenius parameters for rearrangement ($E_a = 3.2$ kcal/mol, $A = 100^{10.0}$ s^{-1}) have recently been reported and are used in our analysis. See: Merrer, D. C.; Moss, R. A.; Liu, M. T. H.; Banks, J. T.; Ingold, K. U. *J. Org. Chem.* **1988**, *63*, 3010. This study was performed in tetrachloroethane. Our deduced Arrhenius parameters obtained in methylene chloride must be considered suspect as the Arrhenius parameters to rearrangment are solvent dependent.

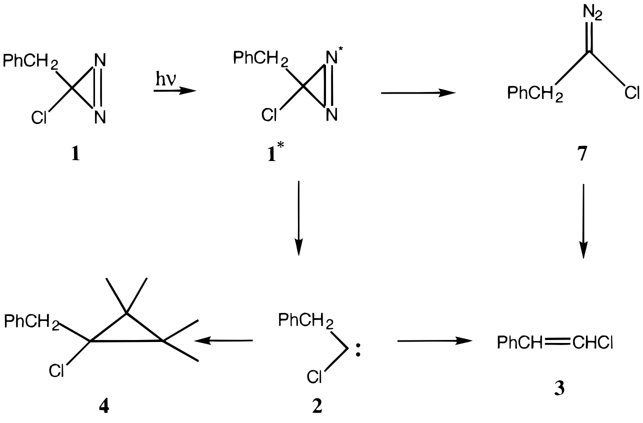
(3) (a) Liu, M. T. H. *Acc. Chem. Res*. **1994**, *27*, 287. (b) Liu, M. T. H.; Stevens, I. D. R. *The Chemistry of the Diazirines*; Liu, M. T. H., Ed.; CRC Press: Boca Raton, FL, 1987; Vol. I, p 111.

S0002-7863(98)00251-0 CCC: $15.00

Scheme 3



Scheme 4

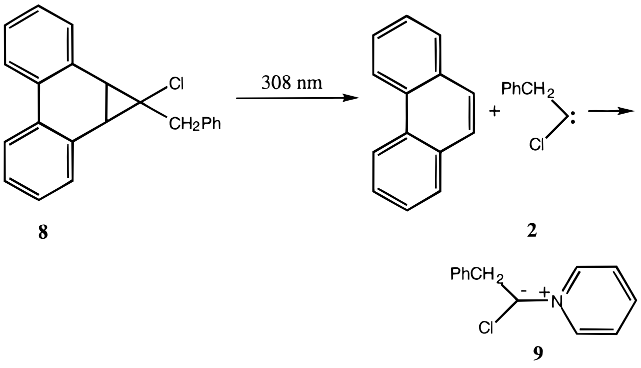


Calculations find that carbene–olefin complexes are not minima but collapse immediately to form cyclopropanes.[5] However, recent experimental and theoretical work indicates that carbenes do form bound complexes with benzene.[6]

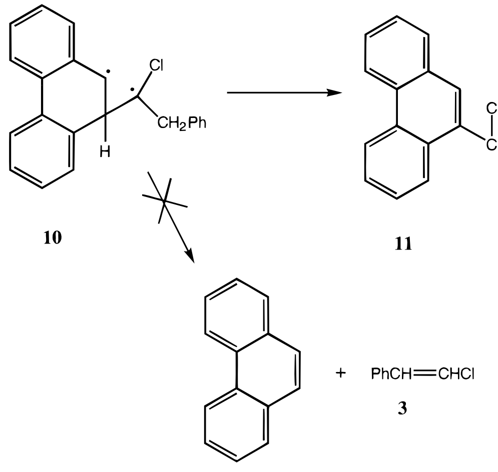
Other interpretations of the data are possible. Following Frey[7] and other early workers in this field, we have attributed the second β-chlorostyrene pathway to either a diazirine excited state[8] (Scheme 3) and/or the decomposition of an unstable diazo compound **7** formed by photoisomerization of diazirine **1**[9] (Scheme 4). Again, following Frey[7] the second pathway to β-chlorostyrene has been associated with an excited state of the carbene by Warner.[10] These schemes also predict curvature of plots of **4**/**3** versus [TME]. The change of the *E*/*Z* ratio of **3** with TME, and the dependence of **3**/**4** versus [alkene] type plots on the nature of the alkene trap, is consistent with the intermediacy of a diazo compound (Scheme 4) that can react with alkenes.[8] It has been suggested that all three pathways may be operating simultaneously in this system.[2,11,12]

To distinguish between these views, an independent precursor to benzylchlorocarbene is needed. If a carbene–alkene complex **5** is the second route to β-chlorostyrenes then the originally reported observations will be independent of precursor, if not the anomalies should disappear. Phenanthrene **8** appeared to us to be a precursor that would allow the differentiation of the various mechanistic proposals.

LFP of **8** produces carbene **2** that can be trapped with pyridine to form ylide **9**.[13]



Obviously **8** cannot form a diazo intermediate. Furthermore, if **8** opens to form biradical **10** upon photolysis, we expect that this biradical (unlike **6**, Scheme 3) will isomerize to **11** rather than somehow form β-chlorostyrene **3**, as the thermal fragmentation of alkylcyclopropanes into a pair of alkenes (via cleavage with rearrangement) is unknown.[14] Thus, we expect that a second pathway to alkene **3** is unlikely when this precursor is employed.



Herein we are pleased to report our studies of the photochemistry of **8**, in the presence and absence of TME. The results are consistent with Scheme 3 and rule out π complex **5** as a

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(4) (a) Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 7131. (b) 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*, 1587.

(5) (a) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555. (b) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291. (c) Blake, J. F.; Wierschke, S. G.; Jorgensen, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 1919.

(6) (a) Khan, M. I.; Goodman, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 6635. (b) Moss, R. A.; Yan, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1998**, *120*, 1088. (c) Jones, M., Jr.; Thamattoor, D. M.; Ruck, R. T. Kyushu International Symposium on Physical Organic Chemistry, December 2–5, 1997, Kyushu University.

(7) Frey, H. M. *Adv. Photochem.* **1964**, *4*, 225.7.

(8) (a) Platz, M. S.; White, W. R., III.; Modarelli, D. A.; Celebi, S. A. *Res. Chem. Intermed.* **1994**, 175. (b) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034. (c) Platz, M. S. *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 2, p 133.

(9) White, W. R., III; Platz, M. S. *J. Org. Chem.* **1992**, *57*, 2841.

(10) Warner, P. M. *Tetrahedron Lett.* **1984**, *25*, 4211.

(11) Bonneau, R.; Liu, M. T. H.; Kim, K. C.; Goodman, J. C. *J. Am. Chem. Soc.* **1996**, *118*, 3829.

(12) Bonneau, R.; Shustov, G. V.; Liu, M. T. H. Kyushu International Symposium on Physical Organic Chemistry, December 2–5, 1997, Kyushu University.

(13) Robert, M.; Likhotvorik, I.; Platz, M. S.; Abbot, S. C.; Kirchoff, M. M.; Johnson, R. *J. Phys. Chem.* **1988**, *102*, 1507.

(14) Gajewski, J. *Thermal Hydrocarbon Isomerizations*; Academic Press: New York, NY 1981.

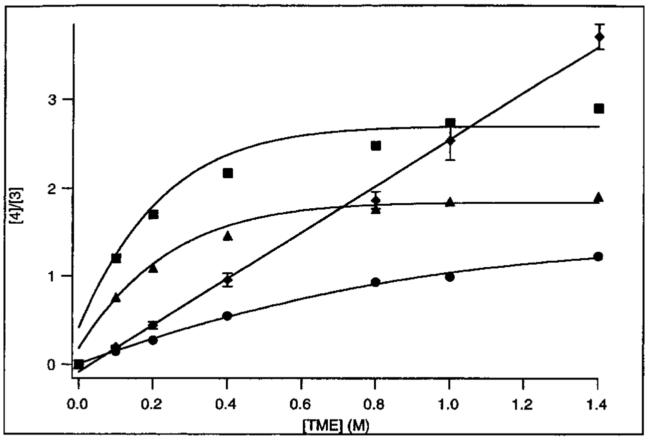

Figure 1. A plot of **4**/**3** vs [TME] obtained at 350 nm from (◆) phenanthrene **8** at 15 °C in CH_2Cl_2, (▲) diazirine **1** at 15 °C in CH_2Cl_2, (●) diazirine **1** at 15 °C in isooctane, and (■) data of Liu[2,3] et al. at 10 °C in isooctane.

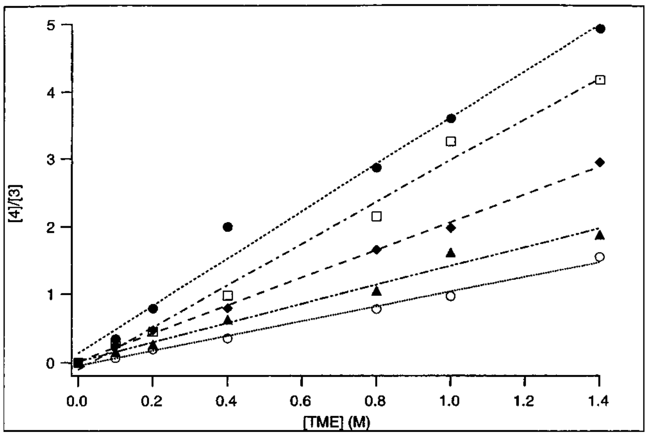

Figure 2. A plot of **4**/**3** vs [TME] obtained from phenanthrene **8** in CH_2Cl_2 at (●) 9, (□) 13, (◆) 23, (▲) 33, and (○) 42 °C at 300 nm. Error bars are not shown but are comparable to those of Figure 1.

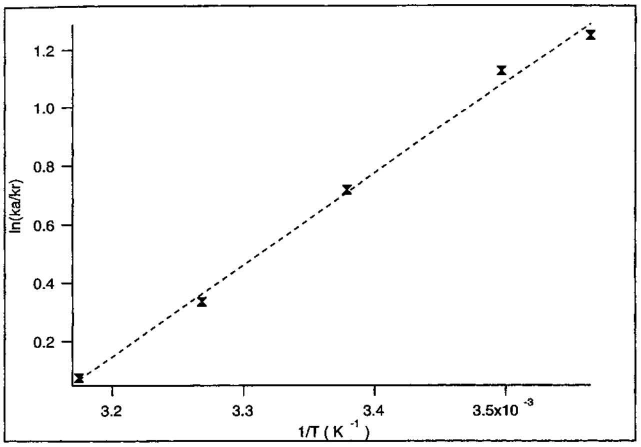

Figure 3. The Arrhenius treatment of the k_A/k_R data obtained by photolysis of **8** in the presence of TME in dichloromethane at 300 nm.

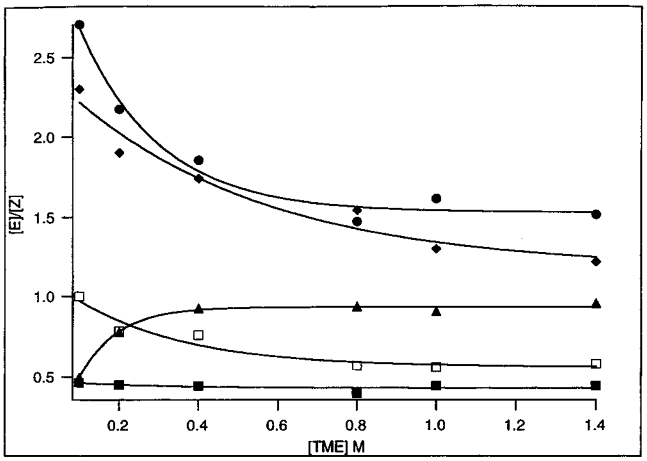

Figure 4. The **E/Z** ratio of the β-chlorostyrenes formed at 15 °C under various conditions: (◆) precursor **8**, 300 nm, CH_2Cl_2; (■) precursor **8**, 350 nm, CH_2Cl_2; (▲) precursor **1**, 350 nm, isoocctane; (□) precursor **1**, 350 nm, CH_2Cl_2; (●) precursor **1**, 350 nm, isoocctane (10 °C), references 2, 11, and 15.

species capable of forming β-chlorostyrene at a rate comparable to its collapse to cyclopropane. The results do not exclude the possibility of the formation of π complex **5**, but such a species, if formed, can only form cyclopropane **4** ($k^c{}_A \gg k^c{}_R$, Scheme 2).

II. Results

We first set out to reproduce the original findings. In our hands, photolysis (320−380 nm, Rayonet Reactor) of diazirine **1** in the presence of TME, in isooctane, produces both styrenes **3** and cyclopropane **4**. A plot of **4**/**3** versus [TME] is curved (Figure 1). The slight difference between our findings and those of the earlier workers is likely due to the small (5°) difference in temperature of the two studies or to small variation in GC response factors.

Photolysis of **8** in the presence of TME again produces β-chlorostyrenes **3** and cyclopropane **4**. A plot of **4**/**3** versus [TME] in CH_2Cl_2 can be fit to a straight line over the range of [TME] where such plots obtained with diazirine **1** are curved (Figure 1). Precursor **8** is insoluble in isooctane, hence the change of solvent. The slope of this plot was measured as a function of temperature (Figure 2). A plot of $\log(k_A/k_R)$ versus $1/T$(K) is linear (Figure 3), which provides the differential activation energies $\Delta\Delta E_a = +1.6$ kcal/mol and $A^A/A^R = 10^{-4.3}$ M^{-1}. These can be converted into absolute values $\Delta E^A = 1.6$ kcal/mol and $A^A = 10^{5.7} s^{-1}$ as the corresponding values of the rearrangement have been reported.[2d]

The E/Z Ratio as a Function of [TME]. The *E*/*Z* ratios of the β-chlorostyrenes produced on photolysis were studied as a function of precursor, photolysis wavelength, solvent, and the presence of TME. The data are summarized in Figure 4. The results seem to be sensitive to each experimental parameter.

It was possible to synthesize a 90/10 mixture of **3** *E*/*Z*. The *E*/*Z* ratio varies upon photolysis (280−320 nm) in CH_2Cl_2 at 15 °C (Figure 5) and photolysis (320−380 nm) in CH_2Cl_2 at 15 °C (Figure 5) in the presence of TME. The *E*/*Z* ratio of **3** also changes from 90/10 *E*/*Z* to 50/50 in CH_2Cl_2 and to 33/66 in isooctane upon photolysis in the absence of TME.

Upon photolysis of **3** and TME a photoproduct was formed in small yield. The product was characterized by GC-MS and its cracking pattern was consistent with that of a [2+2] cycloadduct.

Time-Resolved IR Spectroscopy. Laser flash photolysis of diazirine **1** produces a transient with a strong IR absorption at 2044 cm^{-1}. The transient is long-lived ($\tau \gg 200$ μs) and, we believe, associated with diazo compound **7**. LFP of chloropropyldiazirine **12** and **13** produces diazo compounds **14** (2030 cm^{-1}) and **15** (2028 cm^{-1}), respectively.[15]

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[15] Bonneau, R.; Liu, M. T. H. *J. Am. Chem. Soc.* **1996**, *118*, 7229.

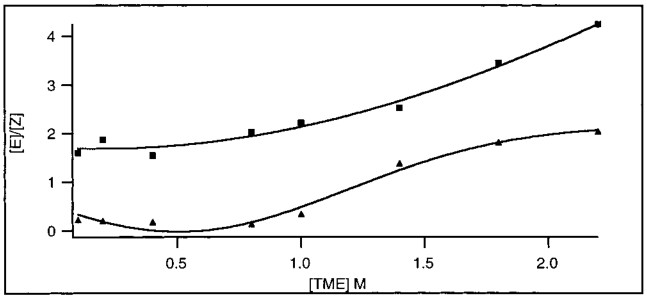
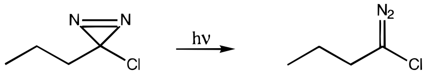
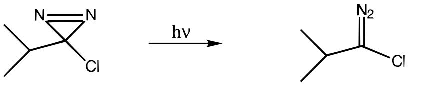


Figure 5. The **E/Z** ratio as a function of [TME] obtained by the photolysis of a 90% *E* isomer of **3** in dichloromethane at 15 °C at (▲) 300 and (■) 350 nm.



12 **14**



13 **15**

Bonneau and co-workers have shown that the quantum yields of the formation of **14** from **12** and diazo compound **15** from **13** are approximately the same (0.10−0.13).[15] Diazirines **1** and **13** were studied under identical conditions. On the basis of the analysis of the IR intensities of diazirine depletion bands and formation of diazo absorption bands we conclude that the quantum yield of diazo formation with benzylchlorodiazirine is 0.075, or about half that of diazirines **12** and **13**.

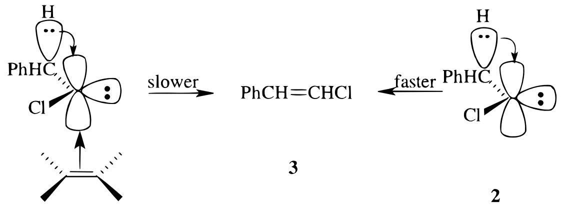
III. Discussion

The curved plots of **4**/**3** first discovered by Tomioka et al.[1] are precursor dependent. Curvature is observed with diazirine **1** but not with phenanthrene **8** over the range of TME concentration employed in the original study. The curvature observed with precursor **1** cannot be due to a complex between carbene **2** and TME that was postulated to form styrene **3** in competition with collapse to cyclopropane **4**.

Many scientists have speculated that carbenes form complexes with alkenes on the way to forming cyclopropanes.[4] The putative complex is formed by the interaction of the empty p-orbital of the singlet carbene with the π electrons of the alkene (Scheme 2).

Theory predicts that these types of complexes are not minima on the potential surface in the gas phase.[5] Our results do not rule out the possibility that a complex such as **5** is formed and has a finite lifetime in solution. However, the data require that if **5** is indeed formed, it must form cyclopropane **3** much faster than it forms **2** plus TME ($k'_A \gg k'_R$).

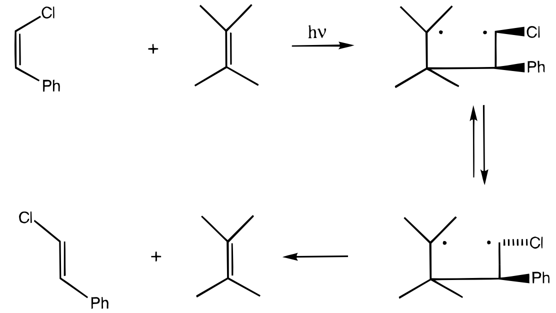
Is this reasonable? We believe it is. Any complex of a carbene and an alkene must be enthalpically stable relative to its free components or it will not be formed. The rearrangement of α hydrogen in a carbene is traditionally viewed as a hydride-like shift where the hydride moves to the empty p-orbital of the carbene carbon. The experimentally determined barrier to this rearrangement is 3.2 kcal/mol.[2d] Complexation must surely raise the barrier to 1,2 hydrogen migration. In contrast, (according to theory)[5] the barrier to collapse of the complex to form cyclopropane is close to zero, if it exists at all. Thus, complexation should make rearrangement even less competitive with cycloaddition as per the Reactivity Selectivity Principle.



5 **3** **2**

From the data of Figures 2 and 3, values of $\Delta E_a^A - \Delta E_a^R = +1.6$ kcal/mol and $A^A/A^R = 10^{-4.3}$ M^{-1} can be deduced. As mentioned previously, it has been reported that $\Delta E_a^R = 3.2$ kcal/mol and $A^R = 10^{10.0}$ s^{-1}.[2e] This indicates that $\Delta E_a^A = 1.6$ kcal/mol, which seems plausible,[16] and that $A^A = 10^{5.7}$ s^{-1}, which seems rather low. It is important to note that the 1,2 migration of the hydrogen reaction is sensitive to solvent and different solvents were used in this study and the absolute kinetic study.

Considering that **3** both photoisomerizes and reacts with TME under our photolysis conditions, we feel it is unwise to attach much significance to the variation of the *E*/*Z* ratio in the presence of TME. **3Z** and **3E** may react with TME at different rates. Furthermore, **3Z** and **3E** may react with TME to form a biradical that can fragment with net isomerization of the alkene. Thus, we feel the variation of the **3** *E*/*Z* ratio with TME is of little mechanistic significance.



Our experiments do not reveal the precise mechanism for the noncarbene pathway operating in diazirines. The second pathway may involve excited states of the carbene[10] or of the diazirine. The latter pathway has been dubbed a "Rearrangement in Diazirine Excited State" (RIES) mechanism.[8,9] According to theory, irradiation of the nπ* band of a diazirine leads to opening of the three membered ring to form a diradical,[17] which we postulate can migrate hydrogen in concert with nitrogen extrusion (Scheme 3). Of all the decay routes possible for diradical **6** this is surely the most exothermic route.[7,8] In principle, biradical **6** can also be formed upon pyrolysis of diazirine **1**.

It is also conceivable that hydrogen migrates in concert with ring opening of the diazirine excited state to form biradical **16**, although this process has not been considered explicitly by theory.

Bonneau *et al.* have made the reasonable suggestion that the importance of the RIES mechanism varies with the structure of the diazirine. In fact, it is claimed that the RIES mechanism accounts for only 6% of the products formed from benzylchlo-

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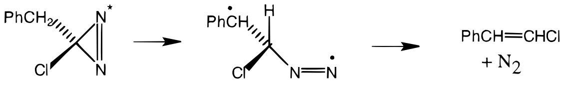
[16] Moss, R. A.; Turro, N. J. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; 213.

[17] (a) Bigot, B.; Ponec, R.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 6573. (b) Müller-Remmers, P. L.; Jug, K. *J. Am. Chem. Soc.* **1985**, *107*, 7275. (c) Yamamoto, N.; Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Wilsey, S. *J. Am. Chem. Soc.* **1978**, *116*, 2064.



16

rodiazirine.[12] It was further stated in this study[12] that the RIES mechanism cannot explain various relative rate measurements.

Photolysis (320−380 nm) of diazirine **1** and phenanthrene **8** in a 1/1 (v/v) mixture of TME and CH_2Cl_2 at ambient temperature leads to ratios of adduct [**4**/(styrenes **3**)] of 2/1 and 16/1, respectively. Under these conditions, nearly all photogenerated carbene should be trapped with TME before it can rearrange,[2,11,15] but this is observed only with precursor **8**. As the quantum yield of diazo formation is 7.5% and the quantum yield of disappearance of diazirines is typically unity,[3] a 26% yield of β-chlorostyrene remains to be explained with diazirine precursor **1**. Although we cannot quantify the importance of RIES to the 26% yield of the noncarbene pathway from our data, we posit that RIES (or an excited state of the carbene[10]) makes a substantial contribution to the second pathway to olefinic product with benzylchlorodiazirine, the PAC[11] data notwithstanding.

IV. Conclusions

The curved plots of (carbene adduct)/(carbene-rearrangement product) versus carbene trapping agent, tetramethylene [TME], reported by Tomioka et al.[1] with benzylchlorodiazirine **1** have been reproduced. However, using a non-nitrogenous precursor, plots of this type are linear over the range of [TME] used in the original study. Thus, any complex formed between benzylchlorocarbene and TME must collapse to form cyclopropane faster then it can fragment with rearrangement to β-chlorostyrene and TME. The anomalous behavior observed when benzylchlorodiazirine is used as precursor can be interpreted without recourse to the existence of carbene−alkene complexes. We posit that rearrangements proceed in the diazirine excited state, although other explanations are possible. Diazirine **1** does photoisomerize to diazo compound **7**, but this process is inefficient ($\phi = 0.075$) and is not likely to be responsible for the curvature in plots of adduct/styrene versus [TME] observed with the diazirine precursor.

V. Experimental Section

The synthesis of phenanthrene **8**,[13] diazirine **1**,[2,15] β-chlorostyrene **3**,[18,19] and cyclopropane adduct **4**[2,15] have all been reported.

Photolysis of 1 in Isooctane. 3-Chloro-3-benzyldiazirine (**1**, 20 mM) in isooctane was photolyzed at 320−380 nm with use of a rayonet reactor equipped with RPR 350 bulbs at 15 °C in the presence of varying amounts of tetramethylethylene (TME) ranging from 0.1 to 2.2 M. The solutions were degassed before the photolysis. The photolytic reaction gave the carbene trapped product 1-benzyl-1-chloro-2,2,3,3-tetramethylcyclopropane (**4**) and the 1,2 H-migration produced (*E*)- and (*Z*)-chlorostyrenes (**3**).

Photolysis of 1 in Dichloromethane. 3-Chloro-3-benzyldiazirine (**1**, 20 mM) in dichloromethane was photolyzed at 320−380 nm with use of a rayonet reactor equipped with RPR-350 bulbs at 15 °C in the presence of varying amounts of tetramethylethylene (TME) ranging from 0.1 to 2.2 M. The solutions were degassed before the photolysis. The photolytic reaction gave the carbene trapped product 1-benzyl-1-chloro-2,2,3,3-tetramethylcyclopropane (**4**) and the 1,2 H-migration produced (*E*)- and (*Z*)-chlorostyrenes (**3**).

Photolysis of 8 in Dichloromethane. 1-Benzyl-1-chloro-1a,9b-dihydrocyclopropa[1]phenanthrene (**8**, 20 mM) in dichloromethane was photolyzed at 320−380 and 280−320 nm with use of a rayonet reactor equipped with RPR-350 and RPR-300 bulbs, respectively, at 9, 13, 23, 33, and 42 °C in the presence of varying amounts of terামethylethylene (TME) ranging from 0.1 to 1.4 M. The solutions were degassed before the photolysis. The photolytic reaction gave the carbene-trapped product 1-benzyl-1-chloro-2,2,3,3-tetramethylcyclopropane (**4**) and the 1,2 H-migration produced (*E*)- and (*Z*)-chlorostyrenes (**3**).

Photolysis of 3 in Dichloromethane. 20 mM solutions of 90% **3E** in dichloromethane were photolyzed at 320−380 and 280−320 nm using a rayonet reactor equipped with RPR-3000 and RPR-3500 bulbs, respectively, at 15 °C in the presence of varying amounts of tetramethylethylene (TME) ranging from 0.1 to 2.2 M. The solutions were degassed before the photolysis.

GC-MS Protocols. Products **3** and **4** were identified by NMR and GC-MS analysis. The relative yields of products were analyzed on a HP 6889 GC with use of a 30m × 0.25 mm × 0.25 μm column packed with 5% PH ME Siloxane and HP 5973 MS detector. The peak area ratio **3**/**4** was multiplied by a response factor of 2.92 to convert into a molar ratio.

Time-Resolved Infrared Protocols. TRIR experiments were performed following the method of Hamaguchi and co-workers.[20] This method allows access to the entire mid-IR spectrum (4000−800 cm^{-1}) with high sensitivity and sufficient time (ca. 50 ns) and frequency (4−16 cm^{-1}) resolution to probe a wide range of transient intermediates in solution. The broadband output of a newly developed $MoSi_2$ infrared source (JASCO) is crossed with excitation pulses (355 nm, 10 ns, 0.6 mJ) from a Continuum HPO-300 diode-pumped Nd:YAG laser. Changes in infrared intensity are monitored by a MCT photovoltaic IR detector (Kolmar Technologies, KMPV11−1-J1), amplified by an NF Electronic Instruments 5305 low noise amplifier, and digitized with a Tektronix TDS520A oscilloscope. Data are collected at a repetition rate of 200 Hz, the maximum data handling speed of our digitizing oscilloscope, and acquisition is synchronized with the stepwise scan of a JASCO TRIR-1000 dispersive spectrometer. To obtain spectra with sufficient sensitivity, several thousand laser shots are typically signal averaged at each IR frequency of interest. Since data are collected at relatively high repetition rates, a flowing cell is necessary to prevent excessive sample decomposition. A reservoir of ca. 15 mL of solution is continually circulated between two calcium fluoride salt plates.

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