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Laser Flash Photolysis Study of Alkylhalocarbenes Generated from Non-Nitrogenous Precursors

Marc Robert, Igor Likhovvorik, and Matthew S. Platz*

Newman and Wolfrom Laboratory of Chemistry, The Ohio State University, 100 W. 18th Avenue, Columbus, Ohio 43210-1173

Sarah C. Abbot, Mary M. Kirchhoff, and Richard Johnson*

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

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Previously we have studied the photochemistry of alkylchlorodiazirines using laser flash photolysis methods and the pyridine ylide technique (White et al. *J. Org. Chem.* **1992**, *17*, 2841). The yield of trappable carbene was found to be a sensitive function of the alkylcarbene structure. This was attributed to ring opening of the diazirine to form a biradical which could suffer rearrangement, in addition to fragmentation to a carbene. It was also possible to explain the data in terms of a carbene–pyridine complex which can either rearrange or collapse to an ylide. In this work, alkylchlorocarbenes are generated from phenanthridenes. The results do not rule out the intermediacy of a carbene–pyridine complex; however, if this species is formed, it does not rearrange to chloroalkene in competition with collapse to form an ylide. This study reduces the urgency with which to postulate carbene–olefin complexes (Tomioka et al. *J. Am. Chem. Soc.* **1984**, *106*, 454).

I. Introduction

Tomioka, Liu, Bonneau (TLB), and co-workers have extensively studied the decomposition of benzylchlorodiazirine (**1**).¹ In alkane solvents, the major decomposition products are (E) and (Z) β -chlorostyrenes **2**, apparently derived from benzylchlorocarbene by 1,2 migration of hydrogen (Scheme 1).

In the presence of a carbene trap such as tetramethylethylene a cyclopropane adduct **3** is formed. These results can be explained using the simple mechanism pictured in Scheme 1.

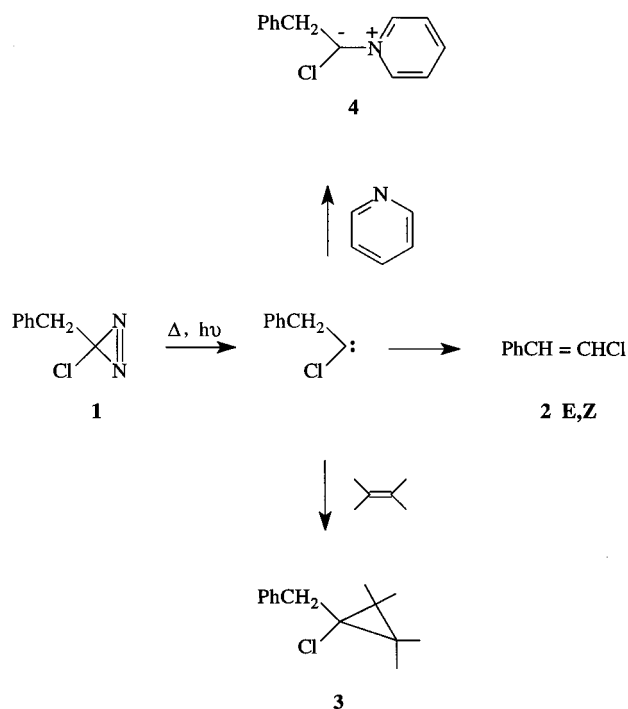
A plot of the yield of **3/2** versus [TME] is not linear. Furthermore the E/Z ratio of β -chlorostyrene products varies as a function of [TME]. Both of these observations are inconsistent with Scheme 1.

As noted by the original investigators, the data require that there must be at least two pathways that form β -chlorostyrenes. The second route to β -chlorostyrenes was associated with a carbene–olefin complex (COC) which can collapse to form adduct **3**, or rearrange to **2**, but with an E/Z signature different from that of a free carbene (Scheme 2). Calculations do not, however, support the intermediacy of a carbene–alkene complex. The COC is not calculated to be a minimum on the potential energy surface.²

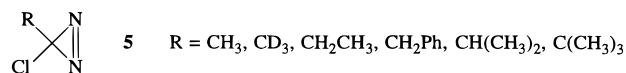
It is important to note that the need for two pathways that can form stable products when diazirines are decomposed was first noted over 30 years ago. This conclusion followed from the discovery that different modes of diazirine decomposition lead to very different product mixtures.³

Several groups have studied the photochemistry of alkylchlorodiazirines using the laser flash photolysis (LFP)–pyridine ylide technique.^{1,4} In this experiment, an alkylchlorodiazirine is excited with a pulse from an excimer laser (XeF, 351 nm). The photochemically prepared carbene is trapped by pyridine to form an ylide (e.g., **4**, Scheme 1). These types of ylides are easily detected because of their intense absorption and relatively long lifetimes.⁴ In our work, the yield of ylide (A_y) was measured optically as a function of pyridine concentration. The yield grows smoothly as [pyridine] increases from zero and then reaches a maximum ($A_{y\infty}$). At these high concentrations of

SCHEME 1

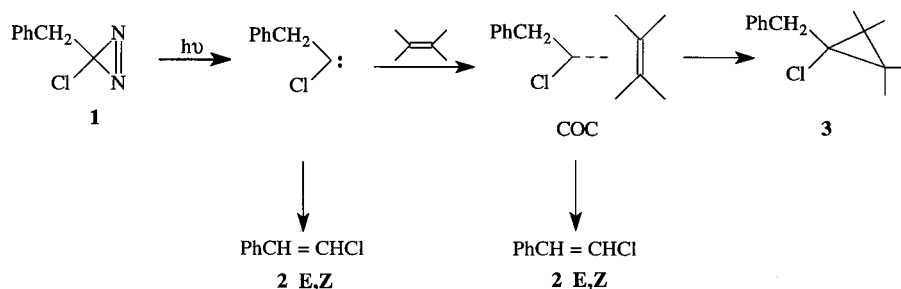


pyridine, we assumed that every carbene produced in the laser pulse was intercepted by pyridine. Under these conditions ylide formation is much faster than all other possible processes that can consume the carbene.⁵ Values of $A_{y\infty}$ were determined for a series of diazirines **5**.

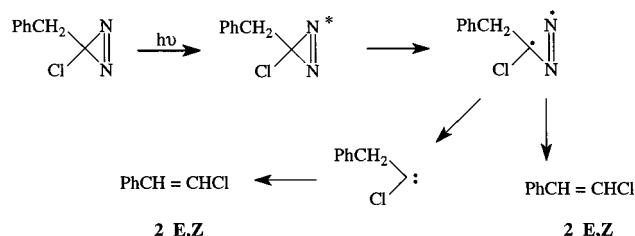


It was determined that the values of $A_{y\infty}$ were strongly dependent on the strength of the C–H bond alpha to the diazirine moiety. These data can be explained, following TLB,

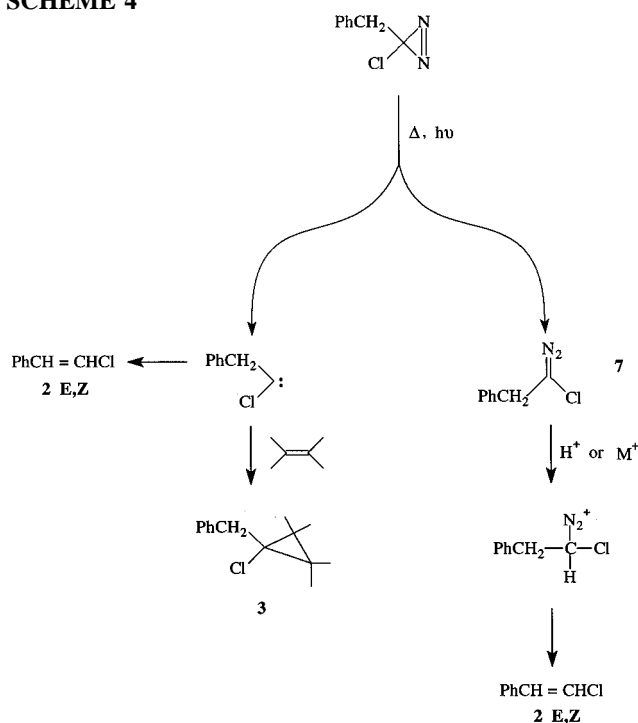
SCHEME 2



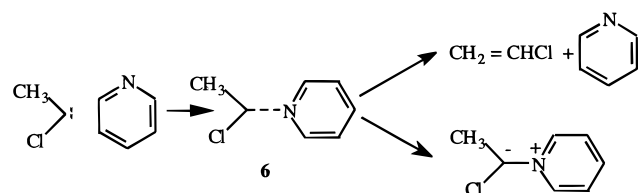
SCHEME 3



SCHEME 4

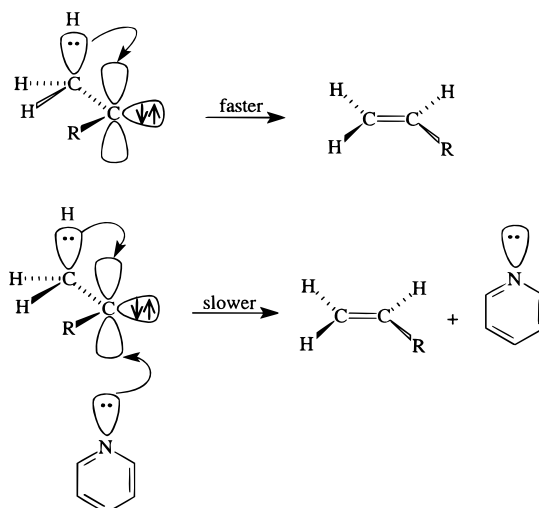


as the result of the formation of a carbene–pyridine complex **6**, which can partition between ylide formation and 1,2 rearrangement of hydrogen.



Nevertheless, we identified the diazirine excited state as the branching point (Scheme 3).^{5,6} In this proposed mechanism the diazirine excited-state C–N bond cleaves to form a biradical.⁷ The biradical partitions between carbene formation and isomerization to alkene in concert with nitrogen extrusion. Thus, we have associated the second pathway with the biradical/excited

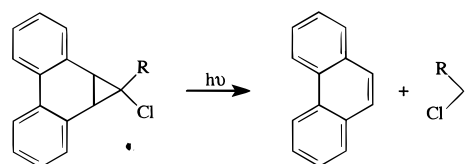
state. This pathway has been dubbed “rearrangement in excited states” or RIES.¹ RIES is the more economical mechanism, as photolysis of a diazirine necessarily produces an excited state. Furthermore, it is our intuition that donation of a lone pair of electrons into the empty p orbital of a carbene as in a pyridine–carbene complex would provide kinetic as well as thermodynamic stabilization and reduce the rate of 1,2 hydrogen shift relative to a free intermediate.⁸ Thus it has been our view that a 1,2 hydrogen shift in the putative complex should not be competitive with the collapse of a complex to the eventual stable product.



We also noted that it was possible to explain the TLB results by isomerization of benzylchlorodiazirine to diazo compound **7**.^{5,6} Decomposition of **7** by ionic pathways can lead to β -chlorostyrenes **2** with a unique E/Z signature and eliminate the need to invoke carbene–olefin complexes (Scheme 4) to explain the data.

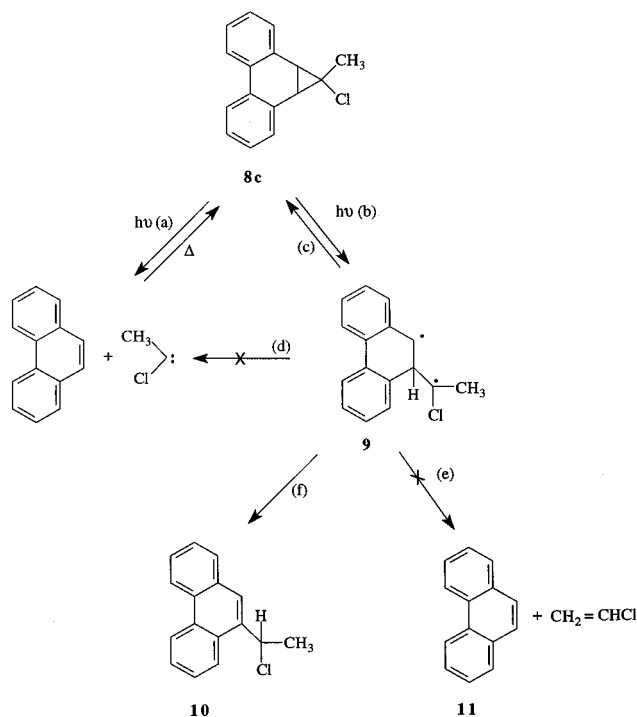
Thus, it seems clear that non-nitrogenous precursors of alkylchlorocarbenes would be extremely useful in clarifying and distinguishing the different mechanistic views that have been proposed.

Phenanthridene compounds have been used successfully to study chloro-⁹ and dichlorocarbenes¹⁰ and will be shown here to be useful sources of alkylchlorocarbenes. Related compounds provide a useful source of dibromocarbenes.¹¹



- 8** R = (a) H (b) Cl (c) CH₃ (d) CD₃ (e) CH₂CH₃
(f) CH₂Ph (g) CH(CH₃)₂ (h) C(CH₃)₃

SCHEME 5



It is possible, of course, that these precursors fragment to form biradicals (path b, Scheme 5) in competition with the concerted cleavage of two bonds to form carbene and phenanthrene (path a, Scheme 5). However, there are two important differences between the biradicals of Schemes 3 and 5. It seems very unlikely, on thermodynamic grounds, that biradical **9** will fragment to carbene and phenanthrene (path d) or mimic the free carbene and fragment to phenanthrene plus vinyl chloride (path e), which corresponds to the key postulate of Scheme 3 (hydrogen migration in concert with fragmentation).¹² The likely fate of biradical **9** should be cyclization to reform starting material (path c) or 1,2 hydrogen shift to form a 9-substituted phenanthrene (**10**, path f).

Thus, with precursors of the type **8**, there should be no second pathway to phenanthrene or to the products of carbene rearrangement (e.g., **11**). Furthermore, there is also no possibility of the rearrangement of **8** to a diazo compound and there seems no facile route to form a species capable of ionic reactions that will form **11**.

Herein we are pleased to report laser flash photolysis studies of phenanthridene precursors of alkylchlorocarbenes. The results of this study do not argue for or against the existence of a carbene-pyridine complex. However, our experimental data rule out the intermediacy of carbene-pyridine complexes (e.g., **6**) which partition between ylide formation and 1,2 hydrogen migration. This does not discredit the postulation of a carbene-olefin complex¹ which can migrate hydrogen or form cyclopropane but does reduce the urgency with which to embrace this concept.

II. Experimental Section

All commercial materials were used without further purification. Reactions were performed under an argon atmosphere. THF was distilled from sodium benzophenone ketyl immediately before use. Melting points are uncorrected. Exact mass was determined using a Kratos MS-30 instrument.

Synthesis. 1-*exo*-methyl-1-*endo*-chloro-1a,9b-dihydrocyclopropa[1]phenanthrene (8c**).** A solution of 1,1-dichloro-

1a,9b-dihydrocyclopropa[1]phenanthrene (1.50 g, 5.8 mmol) in THF and ether (25 mL, 3:2 v/v) was cooled to -78°C . *n*-Butyllithium in hexanes (11.0 mmol) was added dropwise, whereupon the mixture became dark forest green. After 1 h, methyl iodide (1.1 mL, 18.0 mmol) was added. The reaction was kept at -78°C for an additional 1 h and then allowed to warm slowly to room temperature and stirred overnight. Quenching with brine, ether extraction, and concentration afforded a yellow solid. The crude product was purified by rotary chromatography on silica gel, eluted with 2:100 v/v ether/hexane. The resulting white solid was recrystallized twice from hexane to give white crystals assigned as **8c** (0.73 g, 53%). Data included: mp $116-118^\circ\text{C}$; ^1H NMR (360 MHz, CDCl_3) δ 1.86 (s, 3H), δ 2.65 (s, 2H), δ 7.14–7.34 (m, 6H), δ 7.98 (d, 2H, $J = 7.7$ Hz); ^{13}C NMR δ 24.7, 28.3, 32.3, 122.6, 127.1, 127.5, 130.2, 130.6, 131.5; IR (KBr) 3008, 2960, 2926, 1487, 1447 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{Cl}$: C, 79.82; H, 5.45. Found: C, 80.09; H, 5.77.

1-*exo*- d_3 -Methyl-1-*endo*-chloro-1a,9b-dihydrocyclopropa[1]phenanthrene (8d**).** This was prepared as above, but using deuterated methyl iodide (1 mL, 16.0 mmol, 99.5+ atom % D). Workup and rotary chromatography afforded a white solid, which was recrystallized from hexane to give white fluffy crystals of **8d** (0.77 g, 55%): mp $128-130^\circ\text{C}$; ^1H NMR (360 MHz, CDCl_3) δ 2.73 (s, 2H), δ 7.26–7.39 (m, 6H), δ 8.02 (d, 2H); high-resolution MS calcd for $\text{C}_{16}\text{D}_3\text{H}_{10}\text{Cl}$ 245.0865, found 245.0862.

1-*exo*- d_3 -Ethyl-1-*endo*-chloro-1a,9b-dihydrocyclopropa[1]phenanthrene (8e**).** 1,1-Dichloro-1a,9b-dihydrocyclopropa[1]phenanthrene (1.50 g, 5.7 mmol) in THF and ether (25 mL, 3:2 v/v) was cooled to -78°C and treated with *n*-butyllithium (11.0 mmol). After 1 h, bromoethane (1.3 mL, 17.0 mmol) was added dropwise. The reaction was kept at -78°C for an additional 1 h and then allowed to warm slowly to room temperature with stirring overnight. Workup as above followed by rotary chromatography on silica gel (1:39 v/v ethyl acetate/hexane) afforded a white solid which was recrystallized twice from hexanes to give white crystals (0.60 g, 41%): mp $122-123^\circ\text{C}$. ^1H NMR (360 MHz, CDCl_3) δ 1.22 (t, 3H, $J = 7.2$ Hz), δ 1.95 (q, 2H, $J = 7.2$ Hz), δ 0.67 (s, 2H), δ 7.19–7.35 (m, 6H), δ 8.00 (d, 2H, $J = 7.7$); ^{13}C NMR δ 11.1, 31.8, 35.0, 44.9, 122.8, 127.3, 127.8, 130.4, 130.9, 131.8; high-resolution MS calcd for $\text{C}_{17}\text{H}_{15}\text{Cl}$ 254.0862, found 254.0850.

1-*exo*-Benzyl-1-*endo*-chloro-1a,9b-dihydrocyclopropa[1]phenanthrene (8f**).** As described above, 1,1-dichloro-1a,9b-dihydrocyclopropa[1]phenanthrene¹⁰ (1.48 g, 5.7 mmol) in THF/ether (25 mL) was treated with *n*-butyllithium (11.0 mmol). After 1 h, benzyl bromide (2.1 mL, 18.0 mmol) was added. The reaction was kept at -78°C for an additional 1 h and then allowed to warm slowly to room temperature with stirring overnight. Workup as above gave a yellow solid which was purified by rotary chromatography on silica gel and eluted with 1:4 v/v dichloromethane/hexane. The resulting white solid was recrystallized twice from hexane to give white needles (0.55 g, 31%). mp $123.5-125.5^\circ\text{C}$; ^1H NMR (360 MHz, CDCl_3) δ 2.93 (s, 2H), δ 3.39 (s, 2H), δ 7.27–7.41 (m, 11H), δ 8.02 (d, 2H, $J = 7.5$ Hz); ^{13}C NMR δ 31.2, 43.0, 46.6, 122.7, 126.9, 127.2, 127.7, 128.4, 129.3, 130.3, 130.4, 131.8, 137.6; Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{Cl}$: C, 83.39; H, 5.42. Found: C, 83.79; H, 5.34.

1-*exo*-Isopropyl-1-chloro-1a,9b-dihydrocyclopropa[1]phenanthrene (8g**).** To a solution of 1,1-dichloro-1a,9b-dihydrocyclopropa[1]phenanthrene¹³ (0.579 g, 2.22 mmol) in 4 mL of dry THF was added 2 M isopropylmagnesium chloride in THF

(4.5 mL, 9 mmol) at room temperature. After 21.5 h the mixture was cooled to -78°C , and a 1.5 M chlorine solution in tetrachloromethane (6 mL, 9 mmol) was added over 10 min with intensive stirring. The mixture was allowed to warm to room temperature and concentrated on a rotory evaporator. Flash chromatography on alumina (hexanes) afforded 71 mg of product contaminated with 1-isopropyl and 1,1-diisopropyl-1a,9b-dihydrocyclopropa[*l*]phenanthrenes. This solid was recrystallized from pentane to yield 24 mg of pure white crystalline compound with mp $155\text{--}158^{\circ}\text{C}$. Another crop of crystals was obtained by prep TLC of the mother liquor on silica gel using hexanes as eluent. The combined yield was 44 mg (7.4%): ^1H NMR (CDCl_3) δ 1.21 (d, $J = 6$ Hz, 6H), 1.55 (m, 1H), 2.70 (s, 2H), 7.23–7.42 (m, 6H), 7.92–8.03 (m, 2H); ^{13}C NMR (CDCl_3) δ 18.87, 31.98, 39.34, 48.94, 122.61, 127.00, 127.56, 130.04, 130.66, 131.76; HRMS calcd for $\text{C}_{18}\text{H}_{17}^{35}\text{Cl}$ 268.1019, found 268.1021.

1-*exo-tert*-Butyl-1-chloro-1a,9b-dihydrocyclopropa[*l*]phenanthrene (8h). To a well-stirred suspension of copper(I) chloride (1 g, 10.1 mmol) in 20 mL of THF was added 1.5 M *tert*-butyllithium solution in pentane (14 mL, 21 mmol) dropwise at -50°C . The mixture was allowed to warm to 0°C , stirred for 5 min, and then cooled to -50°C . A solution of 1,1-dichloro-1a,9b-dihydrocyclopropa[*l*]phenanthrene¹³ (0.524 g, 2 mmol) in 6 mL of dry THF was added. The mixture was stirred for 0.5 h at -50°C and then at -20°C for 2.5 h. After this period the mixture was cooled to -78°C in a dry ice/acetone bath, and a 1.5 M chlorine solution in tetrachloromethane (15 mL, 22.5 mmol) was added over 5 min, followed by 5 mL of brine and 3 mL of 10% sodium metabisulfite solution. The organic phase was separated, washed with brine, and concentrated in vacuo. Flash chromatography on silica gel (hexane) yielded 106 mg (18.6%) of the white crystalline compound: mp $145\text{--}149^{\circ}\text{C}$ after recrystallization from carbon tetrachloride-hexane; ^1H NMR (CDCl_3) δ 1.20 (s, 9H), 2.91 (s, 2H), 7.19–7.38 (m, 6H), 7.97–8.08 (m, 2H); ^{13}C NMR (CDCl_3) δ 27.20, 27.80, 36.32, 51.76, 122.61, 127.00, 127.55, 130.09, 131.20, 132.20; HRMS calcd for $\text{C}_{19}\text{H}_{19}^{35}\text{Cl}$ 282.1176, found 282.1181.

Photolysis of 1-*exo*-Methyl-1-*endo*-chloro-1a,9b-dihydrocyclopropa[*l*]phenanthrene (8c) with Cyclohexene. Precursor **8c** (11.0 mg) was placed into each of two quartz test tubes with cyclohexene (5 mL, freshly distilled) and hexane (15 mL), and the tubes were closed and purged with nitrogen for 10 min. One tube was irradiated for 30 min and the second for 1 h at 254 nm in a Rayonet photoreactor. Aliquots were analyzed by NMR, with diphenylmethane added as internal standard. The conversion of starting material to phenanthrene was determined to be 38% for the sample irradiated for 30 min and 58% for the sample irradiated for 1 h. Gas chromatographic analysis of aliquots used 1,2,3,4-tetrahydronaphthalene as internal standard and revealed the formation of the expected cyclopropane adduct. The responses of the *endo*- and *exo*-methylchloronorcaranes were calibrated with authentic samples. The yields of *endo*- and *exo*-chloromethylnorcaranes were determined to be 83.4% (*endo*/*exo* 1.0:1.9) for the 30-min photolysis and 77.5% (*endo*/*exo* 1:2.3) for the 1-h photolysis, on the basis of reacted starting material.

III. Results

Laser Flash Photolysis. The LFP system used at The Ohio State University has been described previously.¹⁴ Samples were exposed to the pulses of a 308-nm laser (XeCl, 17 nm, 150 mJ, Lambda Physik LPX100 excimer laser) at right angles to a

TABLE 1: Absorption Maxima of Ylides **4 in Isooctane Produced by LFP of a Phenanthridene Precursor, Unless Otherwise Noted**

R	λ_{max} (nm)
H	373.5
Cl	385–390
CD_3	360
CH_3	360.5 (360 ^a)
CH_2Ph	369.5 (379 ^a)
CH_2CH_3	368
$\text{C}(\text{CH}_3)_3$	376 (376 ^a)
$\text{C}(\text{CH}_3)_2$	370

^a Values obtained from diazirine precursors.

pulsed 150-W He/Xe arc lamp. Transient spectra were recorded using an EG and G Princeton Applied Research model 1460 Optical Multichannel Analyzer (OMA).

Stock solutions of precursors **8** were typically prepared with an optical density ~ 0.5 at 308 nm. A constant volume of the stock solution was added to Suprasil quartz cuvettes. To each cuvette was added varying amounts of pyridine. Solvent was added to each cuvette to maintain a constant volume of sample throughout the experiment. Samples were degassed by purging with dry, oxygen-free argon for 3–4 min.

Infinite yields of pyridinium ylides **4** were obtained by adjusting the concentration of precursors **8** so that the absorbance of each solution closely match ($\pm 1\%$ variation over the whole set of starting compounds) at 308 nm. Pyridine concentration was adjusted to be above the saturation point. Several transient spectra were recorded at λ_{max} for each ylide; the experiment was repeated several times, and average results are presented in Table 3 and Figure 4. The reproducibility of the A_y^{∞} values was $\pm 10\%$.

Isooctane (Aldrich, 99.8%), cyclohexane (Aldrich, HPLC grade), and cyclooctane (Aldrich, 99+%) were used as received. Pyridine was distilled over CaH_2 and stored over KOH pellets.

Chemical Analysis of Mixtures Formed on Photolysis of Precursors **8.** Solutions of precursors **8** (concentration ≈ 5 mM) were prepared in isooctane in the presence of a standard (dimethylterephthalate, concentration ≈ 5 mM). After degassing and sealing the samples in quartz cuvettes, each was photolyzed in a Rayonet photoreactor fitted with 300-nm bulbs. The samples were irradiated for 50 min and analyzed by capillary GC (Perkin-Elmer 8500 GC equipped with a flame ionization detector). Phenanthrene was identified by comparison with an authentic sample and was in all cases the main product of the photolysis.

GC/MSD mass spectral analyses were performed on a HP-5970B Mass Spectrometer, HP-5890 capillary Gas Chromatograph, and the 1,2 hydrogen shift from biradical intermediate **9** to rearranged structure **10** (Scheme 5) was analyzed. Besides phenanthrene, another peak was detected after photolysis, the area of the second product peak increases when going from methylchlorocarbene to ethylchlorocarbene and finally to isopropylchlorocarbene. GC/MS spectra revealed that this peak accounts for a product that has the same fragmentation pattern as the rearranged product **10**. Phenanthridene precursor shows 5–10% decomposition upon GC injection, which varies with structure. We thus concluded that under irradiation the excited state of the precursor partitions between carbene formation (and concomitantly phenanthrene) and opens to a biradical that rearranges to a substituted phenanthrene product. With methylchlorocarbene and ethylchlorocarbene, the chemical yields of phenanthrene are high and the rearrangement pathway is minor. With isopropylchlorocarbene, the amount of rearranged product is close to the amount of phenanthrene produced (at least in

TABLE 2: Dichlorocarbene and Alkylchlorocarbene Lifetimes in Various Solvents and Absolute Rate Constants of Their Reaction with Pyridine. The Data Were Obtained Using Precursors 8, Except Where Noted Otherwise

solvent	Cl- $\ddot{\text{C}}$ -Cl		Cl- $\ddot{\text{C}}$ -CH ₃		Cl- $\ddot{\text{C}}$ -CH ₂ CH ₃	
	k_{pyr} (M ⁻¹ s ⁻¹)	τ (ns)	k_{pyr} (M ⁻¹ s ⁻¹)	τ (ns)	k_{pyr} (M ⁻¹ s ⁻¹)	τ (ns)
isooctane	7×10^9	~ 10000	7.6×10^9	340 (330 ^a)	8.5×10^9 ^b	7 (10 ^c)
cyclohexane			4.75×10^9	195 ± 10	5.3×10^9 ^d	~ 7
cyclooctane	3.9×10^9	~ 1250	3.8×10^9 ^e	~ 40	4.2×10^9 ^e	~ 4.5

^a Value obtained from diazine precursor (see ref 15). ^b Average of previous values obtained with various alkylchlorocarbenes (see ref 15). ^c Value obtained from diazine precursor (see ref 15). ^d The value of k_{pyr} in this solvent is not known. It will be assumed $k_{\text{pyr}}[\text{in cyclohexane}] = k_{\text{pyr}}[\text{in isooctane}]/1.6$ by analogy with the variation of k_{pyr} between these solvents observed with CMeCl. See ref 15. ^e The value of k_{pyr} in this solvent is not known. It will be assumed $k_{\text{pyr}}[\text{in cyclooctane}] = k_{\text{pyr}}[\text{in isooctane}]/2$ by analogy with the variation of k_{pyr} between these solvents observed with CCl₂ and CClBr₂. See ref 15.

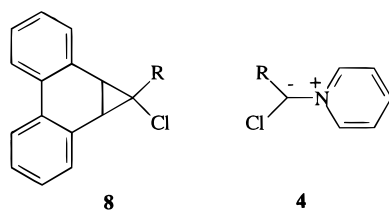
TABLE 3: Yields of Pyridine Ylides Obtained from Diazirines and the Yields of Pyridine Ylides and Phenanthrene Obtained from Phenanthridene Precursors. All Values in a Column Are Relative to Methyl $\equiv 1.0$

substituent R in 8	diazirines ^a A_{y}^{∞}	phenanthridenes ^b A_{y}^{∞}	normalized yield of phenanthrene ^c
<i>tert</i> -butyl	1.9	0.63	0.8–0.75
CD ₃	1.09	0.97 (0.97 ^a)	1
CH ₃	1	1 (1 ^a)	1
CH ₂ Ph	0.75	0.9 (0.85 ^a)	0.85
CH ₂ CH ₃	0.55	0.65 (0.66 ^a)	0.77
H		0.65	
Cl		0.55–0.6	0.75
isopropyl	0.04	0.2	0.5

^a Values obtained in methylene chloride. ^b Values obtained in isooctane. ^c Yields of phenanthrene measured by GC after 50 min of photolysis at 300 nm.

terms of peak area), indicating that both pathways are approximately equally favored.

Laser flash photolysis (308-nm, XeCl excimer laser) of **8a–h**



R = (a) H (b) Cl (c) CH₃ (d) CD₃

(e) CH₂CH₃ (f) CH₂Ph

(g) CH(CH₃)₂ (h) C(CH₃)₃

fails to produce UV–vis active transient intermediates. However, LFP of **8a–h** in the presence of pyridine leads to intensely absorbing transient species (Figure 1, Table 1). These transients are attributed to ylides **4a–g**. This conclusion is supported by the fact that the transient spectra are quite similar to those obtained from the corresponding diazine precursors. Furthermore, the formation of phenanthrene in good yields was demonstrated by gas chromatographic analysis of solutions of **8** exposed to continuous 300-nm radiation.

In certain cases it was possible to resolve the formation of the ylide. In these cases, the ylide was formed in an exponential process, which yielded an observed rate constant, k_{obs} , upon analysis.

The observed rate constant k_{obs} is the sum of $k_{\text{pyr}}[\text{pyridine}]$ and k_0 , the pseudo first-order rate constant associated with the sum of all processes consuming the carbene in the absence of pyridine. As predicated, the plots of k_{obs} versus $[\text{pyridine}]$ are found to be linear, thereby allowing us to extract the rate

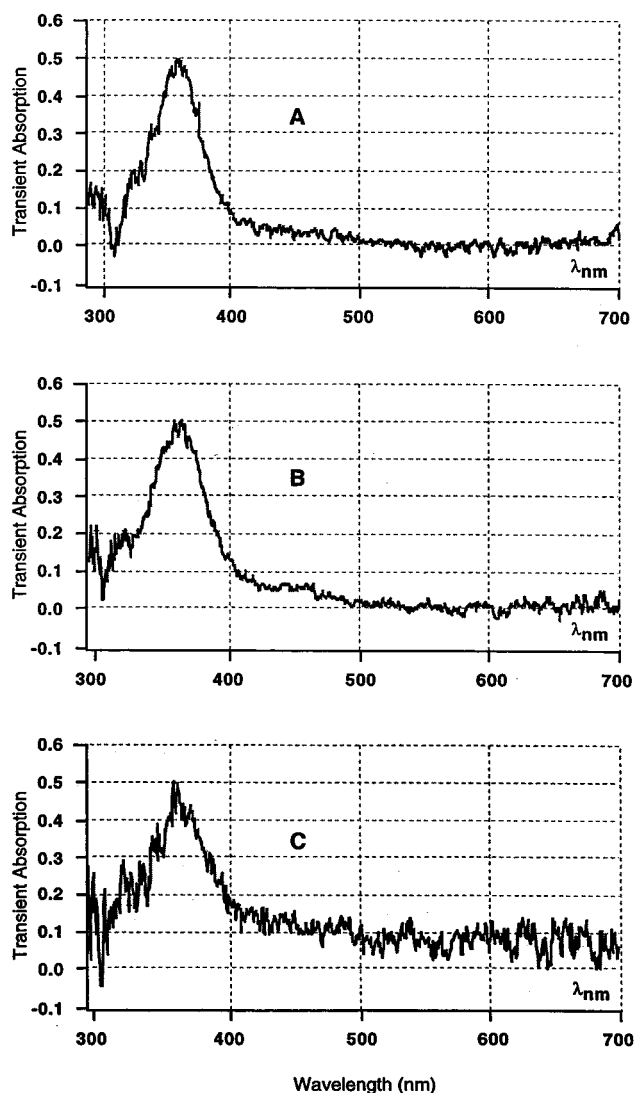


Figure 1. Transient spectra of some selected pyridinium–alkylchlorocarbene ylides produced upon LFP of **8** (A, methylchlorocarbene; B, benzylchlorocarbene; C, isopropylchlorocarbene) in isooctane containing pyridine (A, 0.12 M; B, 0.6 M; C, 0.6 M) at 295 K. The spectra were recorded over a window of 400 ns, approximately 1.2 μ s after laser pulse.

constant of reaction between the carbene and pyridine and the lifetime of the carbene (Figure 2B).

The optical yield (A_{y}) as a function of pyridine concentration was also measured. In the absence of pyridine, A_{y} is close to zero and increases steadily as the concentration of pyridine is increased (Figure 3A). At high concentrations of pyridine, the yield of ylide is saturated (A_{y}^{∞}); every carbene produced in the laser pulse is then trapped prior to reaction with solvent. The

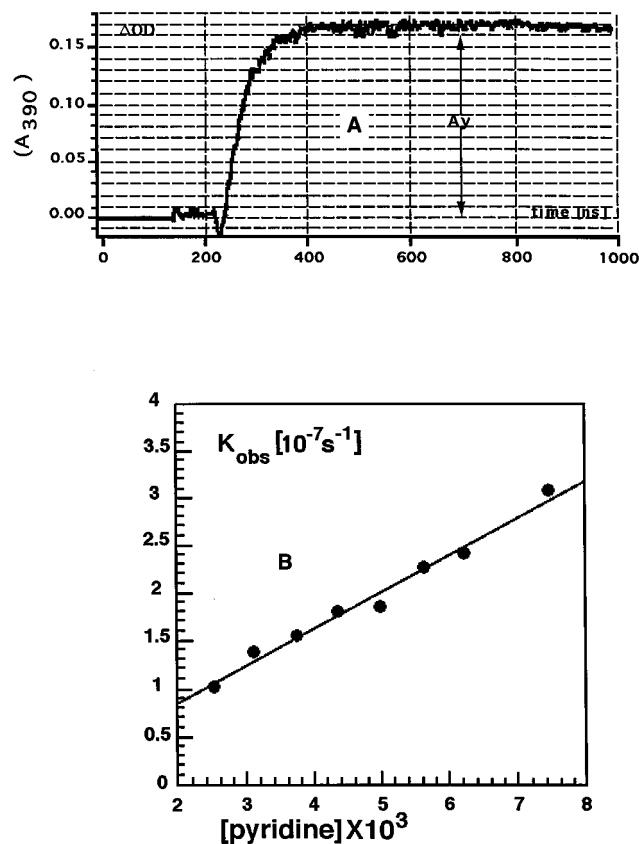


Figure 2. (A) Rate of formation of ylide **4b**, following LFP in cyclohexane containing 0.124 M pyridine at 295 K. (B) Plot of k_{obs} of ylide **4b** versus $[pyridine]$.

quantum yield of ylide formation (ϕ_y) and the optical yield of ylide are given in eq 1, where ϕ_c is the quantum yield of carbene formation, k_{pyr} is the rate constant of quenching by pyridine, and k_0 is a pseudo-first-order rate constant that is the sum of all the processes consuming the carbene in the absence of pyridine.^{4,5}

$$\phi_y = \frac{\phi_c k_{pyr} [pyridine]}{k_0 + k_{pyr} [pyridine]} \quad \text{and} \quad A_y = \phi_y A_y^\infty \quad (1)$$

$$\frac{1}{A_y} = \frac{k_\tau}{\phi_c A_y^\infty k_{pyr} [pyridine]} + \frac{1}{\phi_c A_y^\infty} \quad (2)$$

Thus a plot of $1/A_y$ versus $1/[pyridine]$ is predicted and found to be linear (Figure 3B). Division of the intercept by the slope gives the ratio (k_{pyr}/k_0) , which is equal to $k_{pyr}\tau$, where τ is the lifetime of carbene in the absence of pyridine. After assuming values of k_{pyr} (by comparison to similar carbenes with known rate constants^{1,4}) it was possible to deduce lifetime values for the short-lived ($\tau < 30$ ns) carbenes.

The lifetimes of methylchlorocarbene and ethylchlorocarbene in isooctane determined in this work are in good agreement with previous results (Table 2).^{1,15} There is a tendency for the lifetimes to decrease as solvent viscosity increases. Upon changing from isooctane (viscosity equal to 0.49) to cyclooctane (viscosity equal to 2.2),¹⁶ the methylchlorocarbene lifetime decreases by a factor of approximately 8.5. Dichlorocarbene is a very long-lived carbene.¹⁰ Its lifetime is close to 10 μs in isooctane and is shortened by a factor of approximately 8.5 in the more viscous solvent, cyclooctane. It is difficult to interpret this result because the lifetime of long-lived carbenes can be

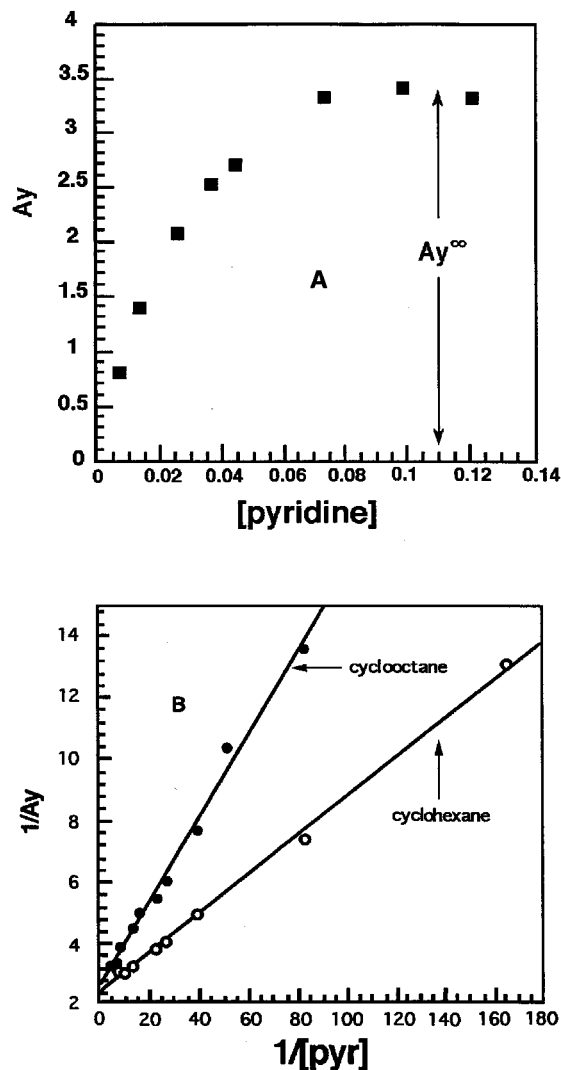


Figure 3. (A) Yield of ylide **4c** as a function of $[pyridine]$ in cyclooctane at 295 K. (B) Double-reciprocal treatment of the data of part A.

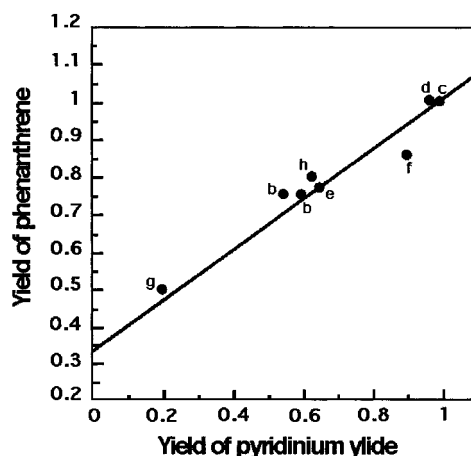


Figure 4. Plot of the yield of phenanthrene versus the yield of ylide **4** obtained from precursors **8b–h** [(b) Cl, (c) CH₃, (d) CD₃, (e) CH₂-CH₃, (f) CH₂Ph, (g) CH(CH₃)₂, (h) C(CH₃)₃].

controlled by reaction with trace amounts of water and oxygen, whose concentration can vary with solvent. Ethylchlorocarbene is an extremely short-lived carbene.¹⁵ The variation of its lifetime with solvent viscosity is small and may be due to experimental error and variation in the value of the rate constant of reaction with pyridine with solvent.

Relative values of A_y^∞ are collected in Table 3 along with the values obtained previously with the diazirine precursors and the yield of phenanthrene obtained upon continuous photolysis of **8a–g** at 300 nm. In each column, the yield of the appropriate quantity obtained with precursors of chloromethylcarbene is defined as unity. Comparisons within a vertical column are meaningful. Comparisons across a horizontal row are useful only in a qualitative sense.

A plot of the yield of phenanthrene versus the yield of pyridine ylides **4b–h** in isooctane is shown in Figure 4. The plot is linear with a slope of 0.65.

IV. Discussion

The yield of ylide **4b–h** varies by a factor of 47.5 from the *tert*-butylchloro- to isopropylchlorocarbene systems using diazirine precursors. This large spread can be attributed to hydrogen migration in a carbene-pyridine complex **6** or to the RIES mechanism (Scheme 3).

The carbene-pyridine complex mechanism predicts that the relative yields of ylide will be independent of precursor. As shown in Table 3, this clearly is not the case. The yield of pyridine ylides derived from precursor **8** varies by only a factor of 3. The dependence of the yield (A_y^∞) of carbene from precursor **8** on the strength of the C–H bond alpha to the carbene center is much less sensitive than that realized from the diazirine precursors. In fact, the *tert*-butyl system, which lacks a migratable hydrogen alpha to the carbene center, gives roughly twice as much carbene, per laser flash, as does methyl, which has such a hydrogen when using the diazirine as the precursor. Yet in the phenanthridene series, the methyl compound **8c** produces more carbene, per laser pulse, than does the *tert*-butyl analogue **8h**. The data demonstrate that carbene-pyridine complexes are simply not responsible for the variation in the yield of ylides realized in LFP experiments. If such complexes are formed, they must collapse cleanly to form the ylide.

The RIES mechanism (Scheme 3) predicts that the yield of ylide will correlate with the yield of phenanthrene (precursors **8b–h**) or nitrogen (diazirines). This correlation is not possible to study with diazirines because nitrogen is a reaction product of both decay routes of the biradical. In the phenanthridene series, phenanthrene should be formed in a stoichiometric yield in pathways that produce a carbene. Indeed, as shown in Figure 4, the yield of phenanthrene does correlate with the yield of carbene. However, the correlation is not perfect. A perfect correlation would have a slope of 1.0. The deviation may be due to the back reaction of carbene with phenanthrene, to reform precursor, the efficiency of which is a function of carbene structure. The deviation may also be due to the aforementioned decomposition of certain precursors during GC analysis.

This study provides no evidence for or against the existence of a carbene-pyridine complex. However, this work provides conclusive evidence against the existence of carbene-pyridine complexes that can rearrange to alkenes in competition with collapse to form ylides. This work does not discredit the mechanism of Scheme 2, in which a carbene-olefin complex partitions between rearrangement and the formation of cyclopropanes. However, it certainly reduces the urgency to embrace this concept.

A definitive proof or disproof of the carbene-olefin complex postulate is available using **8f** and repeating the product analysis

as a function of alkene as in the original study involving diazirines.¹ This work is in progress and will be reported shortly.¹⁷

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