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Laser Flash Photolysis Study of Substituent Effects on the Rate of 1,2-H Migration in a Series of Benzylchlorocarbenes

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Abstract: Laser flash photolysis of para-substituted 3-chloro-3-benzyldiazirines in isooctane produces the corresponding carbenes, which react with pyridine to form ylides or undergo 1,2-H migration to form the (*Z*)- and (*E*)-β-chlorostyrenes. The rate for the 1,2-H migration is determined by plotting the pseudo-first-order rate constants for the growth of the ylide vs [pyridine] and extrapolating to zero pyridine concentration. In the case of (*p*-chlorobenzyl)chlorocarbene, the carbene decay can be monitored directly at 310 nm, whereas in [*p*-(trifluoromethyl)benzyl]chlorocarbene, the 285-nm trace may be analyzed as the sum of the absorption of the carbene and of the product β-chlorostyrenes. A Hammett plot of the logarithms of the rate constants for 1,2-H migration vs σ_p values gave a ρ value of −1.0, consistent with a hydride-like 1,2-H shift to the carbene center. The rate constants for the cyclopropanation of carbenes with tetramethylethylene (TME) were determined. In particular, the cyclopropanation of (*p*-chlorobenzyl)chlorocarbene with TME gave a negative activation energy of −4.7 kcal mol^{-1}.

The intramolecular 1,2-hydrogen migration to a carbene center, affording an alkene, has been a subject of considerable interest.[1] Theoretical calculations[2] of activation energies for 1,2-H shifts in singlet carbenes have been carried out using MP4/6-311G** energies calculated on MP2/6-31G*-optimized geometries. The predicted activation energies for methylchlorocarbene, *cis*- and *trans*-methylhydroxycarbene, *cis*- and *trans*-methylmethoxycarbene, *trans*-methylvinylcarbene, and allylmethylene are 11.5, 24.9, 24.5, 23.1, 26.9, 8.4, and 0.0 kcal mol^{-1}, but these results await experimental confirmation.

Recently, the rate constants and activation parameters for the 1,2-hydrogen shift of alkylchlorocarbenes have been measured.[3] The reported E_a for methylchlorocarbene is approximately half the calculated value.[3f] We obtained a lifetime of ~18 ns for benzylchlorocarbene at ambient temperature both by monitoring the carbene decay directly and by plotting the pseudo-first-order rate constants for growth of the ylide vs pyridine concentration and extrapolating to zero pyridine concentration.[4]

It was suggested from our relative rate studies[5] that 1,2-hydrogen migration is decelerated by electron-withdrawing substituents on the phenyl ring, and we now wish to report the absolute rate constants, k_i, for 1,2-H migration in [*p*-(trifluoromethyl)benzyl]chlorocarbene and (*p*-chlorobenzyl)chlorocarbene measured by following the product growth or the carbene decay in the laser flash photolysis (LFP) of the corresponding diazirines. The rate constants for the reaction of these carbenes with pyridine and tetramethylethylene (TME) will be examined as well.

$$XC_6H_4CH_2\ddot{C}Cl \xrightarrow{k_i} XC_6H_4CH{=}CHCl\ (Z\text{ and }E)$$

$$XC_6H_4CH_2\ddot{C}Cl + \text{pyridine} \xrightarrow{k_y} \text{pyridinium ylide}$$

$$XC_6H_4CH_2\ddot{C}Cl + \text{TME} \xrightarrow{k_q} \text{cyclopropane}$$

$$X = p\text{-}CF_3 \text{ or } p\text{-}Cl$$

Results and Discussion

[*p*-(Trifluoromethyl)benzyl]chlorocarbene (FC). Upon irradiation (350 nm) in isooctane, 3-[*p*-(trifluoromethyl)benzyl]-3-chlorodiazirine (**1**) undergoes dinitrogen extrusion to give *p*-$CF_3C_6H_4CH_2\ddot{C}Cl$ (FC), which rearranges to (*Z*/*E*)-*p*-$CF_3C_6H_4CH{=}CHCl$. In the presence of TME, cyclopropanation competes directly with the intramolecular 1,2-hydrogen migration. LFP of **1** in isooctane with the third harmonic of a mode-locked (200 ps) Nd-YAG laser produces a transient absorption in the 285–300-nm range. This spectrum is similar to that observed for benzylchlorocarbene[4] except that the spectrum due to FC is shifted to lower wavelength and the spectrum due to the product styrene is shifted to higher wavelength such that a transient signal due to the absorption of FC alone was not observed in the 310-nm region. In the 285–295-nm region, the changes in the absorbance are characterized by an "instantaneous" jump of the absorption followed by a growth. The 285-nm trace (Figure 1) may be analyzed as the sum of the absorptions of the carbene FC and of the product β-chlorostyrene, respectively decaying and growing with first-order kinetics (τ = 45 ns, for a diazirine concentration of 20 mM in isooctane at 24 °C).

Although a large body of information exists for carbene reactions using diazirines as precursors, the self-quenching reaction of carbene with diazirine has only recently been reported.[6-8] Thus, the lifetime ($1/\tau = k$) of FC was determined as a function of [**1**].

A plot (Figure 2) of the reciprocal lifetime of FC as a function of [**1**] ranging from 20 to 80 mM yields a rate constant, k_D, of $(2.5 \pm 0.3) \times 10^8$ M^{-1} s^{-1} for the reaction of FC with diazirine. Extrapolating the lifetime to zero diazirine concentration yielded 55 ns for the lifetime of FC.

According to a calculation using the rate constants, k_i and k_D, photolysis of neat diazirine **1** should give exclusively azine if it is assumed that once the ylide intermediate is formed, azine must be produced. However, analysis reveals that the products contained 50% azine and 40% chlorostyrenes. This suggests that the ylide might be susceptible to hydrogen migration, yielding chlorostyrene, or that the ylide could be formed reversibly. These findings are in agreement with the results obtained[9] from the thermal decomposition of diazirine, in which the azine formation was attributed to the carbene association with the diazirine followed by rearrangement.

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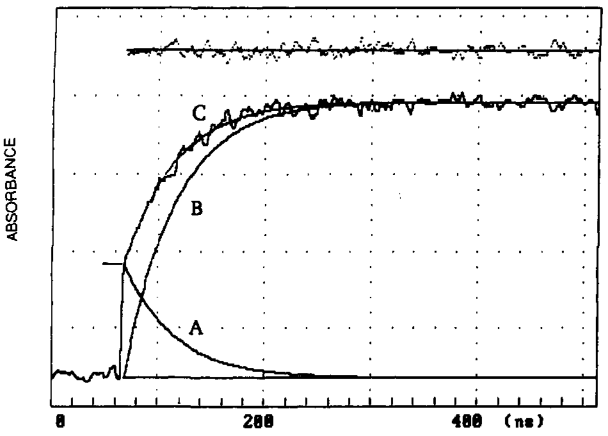

Figure 1. Transient absorption at 285 nm for a solution of 3-chloro-3-[p-(trifluoromethyl)benzyl]diazirine (20 mM) in isooctane at 24 °C analyzed as the sum of the absorption of two species: (A) carbene formed within 3-ns response time of the LFP apparatus and decaying with a 45-ns lifetime; (B) the product styrene (τ growth = 45 ns) formed from the carbene; (C) experimental data fitted with the sum of the two theoretical curves A and B.

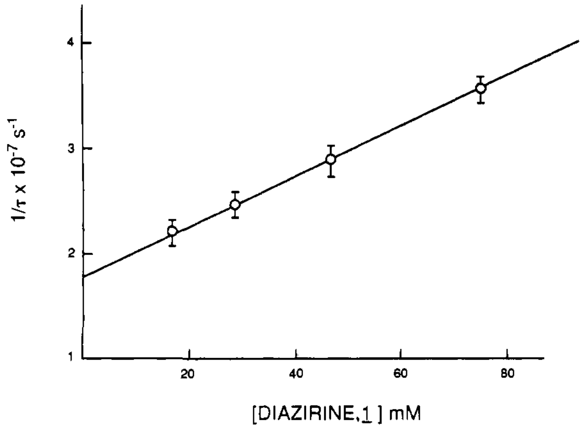

Figure 2. Plot of the reciprocal lifetime of FC (determined by deconvoluting the signal at 285 nm) vs [1] at 24 °C.

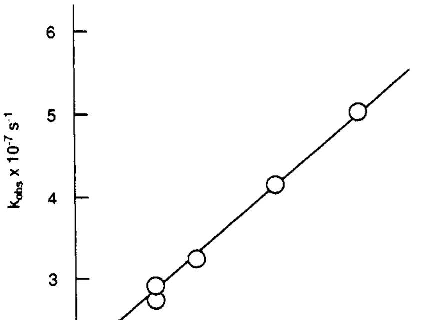

Figure 3. Plot of the observed pseudo-first-order rate constants for growth of the pyridinium ylide absorption at 380 nm vs [pyridine] at 24 °C.

LFP of 20 mM **1** in isooctane at 24 °C in the presence of pyridine produces a transient species at 380 nm. This transient is not present in the absence of pyridine and is attributed to the pyridinium ylide. A plot of the observed pseudo-first-order rate constants for the growth of the absorption at 380 nm vs pyridine concentration is linear (Figure 3). The slope gives the rate constant for the reaction of FC with pyridine, $k_y = (1.35 \pm 0.20) \times 10^{10}$ M^{-1} s^{-1}, and the intercept yields a reciprocal lifetime for FC of τ = 47 ns, in agreement with the previously determined value (τ = 45 ns) as shown in Figure 1.

Table I. Rate Constants (k_i) for 1,2-H Shift in [p-(Trifluoromethyl)benzyl]chlorocarbene and (p-Chlorobenzyl)chlorocarbene as a Function of Temperature

T, °C	τ, ns	$10^{-7}k_i$, s^{-1}	T, °C	τ, ns	$10^{-7}k_i$, s^{-1}
		[p-(Trifluoromethyl)benzyl]chlorocarbene			
2	90	1.11	35	36	2.78
15	60	1.66	47	25	4.00
24	45	2.22			
		(p-Chlorobenzyl)chlorocarbene			
-3	53	1.89	25	24	4.17
-2	51	1.96	29	22	4.55
12	34	2.94	38	17.5	5.71

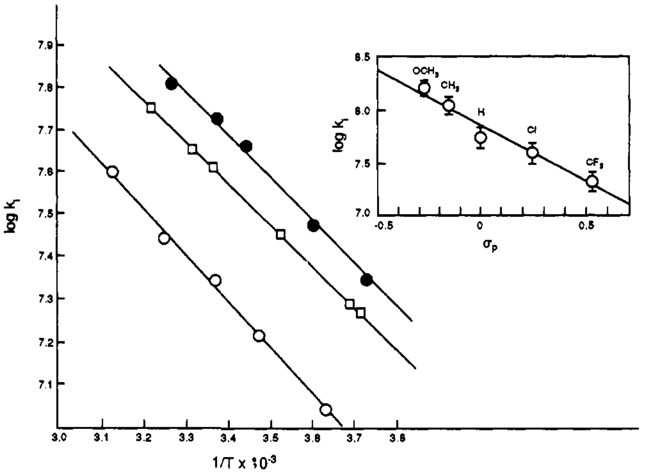

Figure 4. Arrhenius plots of the rate constants for 1,2-H migration: (●) $C_6H_5CH_2\ddot{C}Cl$; (□) p-$ClC_6H_4CH_2\ddot{C}Cl$; (○) p-$CF_3C_6H_4CH_2\ddot{C}Cl$. Insert: Hammett plot for log k_i vs σ_p at 25 °C.

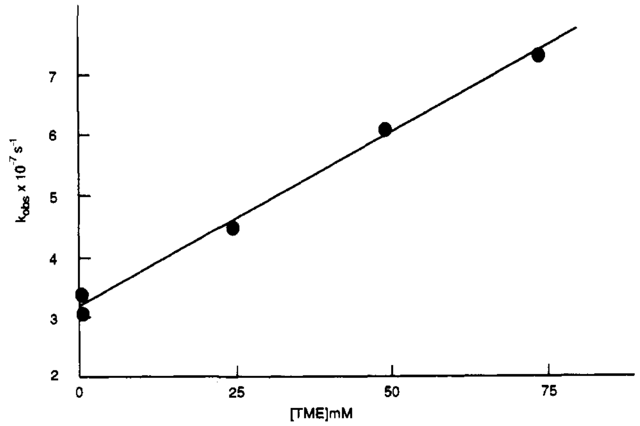

Figure 5. Plot of k_{obs} vs [TME] at 24 °C with [1] = 2.5×10^{-2} M and a constant pyridine concentration of 6×10^{-4} M.

The temperature dependence of k_i was determined by deconvoluting the signal at 285 nm over the 2–47 °C temperature range (Table I and Figure 4). Least-squares analysis of the data in Table I gives the following kinetic parameters:

$$E_i = 4.90 \pm 0.16 \text{ kcal mol}^{-1} \qquad \log A = 10.94 \pm 0.12$$

When a constant amount of pyridine (0.6 mM) is added to 25 mM **1** in isooctane, the transient at 380 nm can be used as a probe to monitor the reaction of FC with other substrates. For example, the addition of tetramethylethylene decreases the yield of ylide formation because the cycloaddition of FC to alkene competes with ylide formation but increases the rate of growth of ylide, $k_{obs} = k_i$(at 25 mM **1**) + k_y[pyridine] + k_q[TME]. Excellent linearity was obtained at 24 °C for k_{obs} vs TME concentration from 20 to 80 mM. The slope in Figure 5 yielded a value of $k_q = (5.7 \pm 0.3) \times 10^8$ M^{-1} s^{-1} for the addition of FC to TME.

(p-Chlorobenzyl)chlorocarbene (CC). Irradiation of 3-chloro-3-(p-chlorobenzyl)diazirine (**2**) in isooctane gives p-$ClC_6H_4CH_2\ddot{C}Cl$ (CC), which rearranges to (Z/E)-p-$ClC_6H_4CH{=}CHCl$, and in the presence of TME, cyclopropanation competes with the formation of styrenes. Thus, the chemistry of CC is similar to that of FC. However, LFP of 25 mM **2** in isooctane produces a transient absorption in the 300–330-nm range. This spectrum is similar to that observed for benzylchlorocarbene[4] and is assigned to (p-chlorobenzyl)chlorocarbene. The extinction coefficient of carbene CC in isooctane at 310 nm was found to be 7.8×10^2 L mol^{-1} cm^{-1}. This was determined by comparing the transient absorbance due to the carbene with that of the triplet–triplet absorption of benzophenone[10] in benzene ($\epsilon = 7.63 \times 10^3$ L mol^{-1} cm^{-1}, $\lambda = 530$ nm). Both species were produced with a quantum yield of unity[11] by excitation of solutions where the concentrations of the diazirine and benzophenone were adjusted to give the same absorption of the laser pulse at 355 nm. By analyzing the first-order decay of the carbene absorption at 310 nm, we determined the rate constant at 29 °C for 1,2-hydrogen migration, $k_i = (4.54 \pm 0.10) \times 10^7$ s^{-1}. As with **1**, LFP of **2** in isooctane in the presence of pyridine gives a new transient absorption in the 350–410-nm range ($\lambda_{max} = 380$ nm). A plot of the observed pseudo-first-order rate constants for growth of the absorption, k_{obs}, at 380 nm vs pyridine concentration is linear. Least-squares analysis of measurements for five different concentrations of pyridine ranging from 0.4 to 2.3 mM yielded the rate constant for ylide formation, $k_y = (1.8 \pm 0.4) \times 10^{10}$ M^{-1} s^{-1} at 29 °C. Each measurement consists of an average of five determinations. The intercept yielded a value of $(4.3 \pm 0.5) \times 10^7$ s^{-1} for k_i. This is in excellent agreement with the k_i obtained from direct observation of carbene decay at 29 °C. By analyzing the first-order decay of carbene absorption at 310 nm, we determined the rate constants for 1,2-hydrogen migration (Table I). The Arrhenius plot, shown in Figure 4, gives an activation energy of 4.50 ± 0.10 kcal mol^{-1} and a pre-exponential factor equal to $10^{10.91 \pm 0.10}$ s^{-1}.

Since the carbene CC can be observed directly, it is possible to examine the rate constant for cycloaddition of CC with TME in isooctane by measuring the rate of decay of the CC absorption at 310 nm, $k_{obs} = k_i + k_q[\mathrm{TME}]$. Least-squares analysis of measurements for four different concentrations of TME ranging from 4 to 25 mM gave the rate constant for cycloaddition, $k_q = (5.50 \pm 0.50) \times 10^8$ M^{-1} s^{-1} at 25 °C. The intercept yielded a value of 4.17×10^7 s^{-1} for k_i. Examination of the kinetics as a function of temperature leads to the following second-order rate constants: 15 °C, $k_q = 7.60 \times 10^8$ M^{-1} s^{-1}; 13 °C, $k_q = 8.31 \times 10^8$ M^{-1} s^{-1}; −3 °C, $k_q = 12.7 \times 10^8$ M^{-1} s^{-1}. As the temperature decreases from +25 to −3 °C, the cyclopropanation rate constant, k_q, increases. Least-squares analysis of log k_q vs $1/T$ gave the values of -4.70 ± 0.50 kcal mol^{-1} and 5.30 ± 0.50 for the activation energy and log A, respectively. As a check of the kinetic data, the LFP data are examined as follows: E(1,2-H shift) − E(cyclopropanation) = 4.50 − (−4.70) = 9.2 ± 0.5 kcal mol^{-1}; A(1,2-H shift)/A(cyclopropanation) = $10^{10.9}/10^{5.3} = 10^{5.6 \pm 0.5}$. This is in excellent agreement with the previously published data on relative rates,[5] in which E(1,2-H shift) − E(cyclopropanation) = 8.7 ± 0.1 kcal mol^{-1} and A(1,2-H shift)/A(cyclopropanation) = $10^{5.2 \pm 0.2}$.

Within error limits, the difference in activation energy and the ratio of the A factors derived from continuous and pulsed irradiation are identical. It is to be noted that values for E(1,2-H shift) − E(cyclopropanation) have been determined for benzylchlorocarbene with various alkenes.[12] These values were 8.1, 6.6, 6.8, 6.3, 5.4, and 6.0 kcal mol^{-1} for tetramethylethylene, butyl vinyl ether, 1-hexene, diethyl fumarate, diethyl mesaconate, and 2-chloroacrylonitrile, respectively. Since the energy of activation for 1,2-H shift in benzylchlorocarbene has been reported to be 4.5 ± 0.3 kcal mol^{-1}, it follows that the activation energies for the cyclopropanation of benzylchlorocarbene to the above alkenes are from −1 to −4 kcal mol^{-1}.

Negative activation energy for cyclopropanation can be explained in terms of a carbene–alkene complex proposed by Turro and Moss[13] to account for the negative activation energy observed for the addition of $Ph\ddot{C}Cl$ to TME ($E_a = -1.7$ kcal mol^{-1}). However, Houk and Rondan[14] have advanced an alterative interpretation that negative activation energies can arise in fast reactions because $\Delta S^{\ddagger}$ is large and negative, such that the temperature dependence of the free energy barrier is entropy controlled. The salient feature of the present data is that the observed activation energy for cyclopropanation is negative by nearly 5 kcal mol^{-1}, i.e., approximately 3 kcal mol^{-1} more negative than that measured for the addition of TME to $Ph\ddot{C}Cl$. Since these measurements are conducted in solution where the effect of temperature on the diffusion rate introduces a positive "activation energy" for intermolecular reactions, the effective value of E_a is even more negative and is in the range −6 to −6.5 kcal mol^{-1}. The mechanism of the cycloaddition of $C_6H_5CH_2\ddot{C}Cl$ to TME has been discussed extensively in our recent paper.[4] In it, we concluded that time-resolved laser flash spectroscopy is unable to prove or disprove the existence of a carbene–alkene complex, but its existence is consistent with all kinetic and spectroscopic results obtained by LFP.

The complex model is particularly useful because it provides a way to rationalize the variations of the Z/E ratio of chlorostyrenes vs TME concentration and the fact that the ratio chlorostyrenes/cyclopropane extrapolated to infinite olefin concentration depends on the nature of the olefin.[4] Alternative models have been proposed involving excited carbene, formation of a diazo intermediate from the excited diazirine, or formation of azine followed by subsequent photolysis. These may be able to account for the variation of the Z/E ratio and the linear relation between chlorostyrenes/cyclopropane and 1/[olefin], but they all predict that the intercept of these linear plots will be independent of the nature of the olefin. Furthermore, the role of an excited carbene seems highly improbable for reaction in solution under continuous irradiation. The yield of azine formation from carbene + diazirine is very small under the usual experimental conditions. With [diazirine] = 10^{-2} M and [olefin] $\simeq$ 0.1–0.5 M and with the known rate constants, the yield of azine formation is only 3% at the initial stage of the photolysis and decays to zero as the diazirine disappears.

Relative-rate studies on substituted 3-chloro-3-benzyldiazirines in alkenes to yield cyclopropanes and chlorostyrenes have been reported.[5] These results suggest that the cyclopropanation of benzylchlorocarbenes is independent of substituents on the phenyl ring. This conclusion is now substantiated by the absolute rate constants for cycloaddition of benzylchlorocarbene,[4] FC, and CC with TME, for which the k_q values are 6.2×10^8, 5.7×10^8, and 5.5×10^8 M^{-1} s^{-1}, respectively. Assuming that the cyclopropanation rate constants, k_q, are very similar for all the substituted benzylchlorocarbenes and close to 5.8×10^8 M^{-1} s^{-1}, the k_i values can be calculated for p-$CH_3OC_6H_4CH_2\ddot{C}Cl$ and p-$CH_3C_6H_4CH_2\ddot{C}Cl$ since the k_i/k_q ratios (0.293 and 0.205) are known[5] at 24 °C. Thus, the rate constants for 1,2-H migration, k_i, for p-$CH_3OC_6H_4CH_2\ddot{C}Cl$ and p-$CH_3C_6H_4CH_2\ddot{C}Cl$ are estimated to be 1.7×10^8 s^{-1} and 1.2×10^8 s^{-1}, respectively.

It is clear that 1,2-hydrogen migration is accelerated by OCH_3 or CH_3 substituents and is decelerated by Cl or CF substituents on the phenyl ring. The decreasing values of k_i in the order p-MeO > p-Me > H > p-Cl > p-CF_3 reflect the effects of substituents in the aryl group. The Hammett plot (Figure 4 insert) for log k_i vs σ_p values gives a ρ value of approximately −1.0. The negative ρ value is consistent with the hydride-like character of the 1,2-H

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shift to the carbenic center. There is a 7-fold increase in lifetime from $p\text{-MeOC}_6\text{H}_4\text{CH}_2\ddot{\text{C}}\text{Cl}$ to $p\text{-CF}_3\text{C}_6\text{H}_4\text{CH}_2\ddot{\text{C}}\text{Cl}$. This effect is much smaller than the magnitude predicted by theoretical calculations,[2] but this is to be expected. The substituent effect is obviously less when the substituent is placed on the phenyl ring, as in our case, rather than on the carbene center, as considered in the theoretical study. Nevertheless, the present work represents a first quantitative study of the substituent effect on 1,2-H shift to a carbene.

Experimental Section

3-[*p*-(Trifluoromethyl)benzyl]-3-chlorodiazirine (**1**) and 3-(*p*-chlorobenzyl)-3-chlorodiazirine (**2**) were prepared by Graham's method[15] and purified by chromatography on silica gel.

Product Studies: Photolysis of Diazirine 1 in TME. Diazirine **1** (3×10^{-3} mol) and TME (3×10^{-2} mol) were dissolved in isooctane (40 mL), and the solution was photolyzed (350 nm) for 30 h at 25 °C. The unreacted TME and solvent were distilled off under reduced pressure. The residue was chromatographed on a column of silica gel and eluted with hexane containing 2% ethyl acetate. The products were (*Z*)- and (*E*)-$p\text{-CF}_3\text{C}_6\text{H}_4\text{CH}{=}\text{CHCl}$ (30%) [MS *m/e* 208 (33), 206 (100, M^+), 171 (94)] and 1-chloro-1-[*p*-(trifluoromethyl)benzyl]-2,2,3,3-tetramethylcyclopropane (65%) [MS *m/e* 290 (2), 271 (10), 255 (100); ^{1}H NMR (CDCl_3) δ 1.10 (s, 6 H, CH_3), 1.20 (s, 6 H, CH_3), 3.15 (s, 2 H, CH_2), 7.1–7.6 (m, 4 H, Ar H)]. Authentic samples of the styrene and cyclopropane were used to calibrate the gas chromatograph, and the absolute yields of the products were determined from the integrated areas of the components in the GC analysis. Bibenzyl was used as the GC internal standard. It is to be noted that no azine was formed under the above experimental conditions.

Photolysis of neat diazirine **1** yielded chlorostyrene (40%) and the expected azine (50%), $(p\text{-CF}_3\text{C}_6\text{H}_4\text{CH}_2\text{CCl}{=}\text{N}{-})_2$ [MS *m/e* 440 (10, M^+), 159 (100); UV broad absorption 250–350 nm ($\epsilon \sim 10^4$)]. The product analysis[5] for diazirine **2** and the laser flash photolysis setup[4] have been described previously.

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Registry No. **1**, 139913-92-1; **1** azine derivative, 139913-96-5; **2**, 91309-66-9; fluoro[*p*-(trifluoromethyl)benzyl]carbene, 139913-93-2; (*E*)-1-chloro-2-[*p*-(trifluoromethyl)phenyl]ethene, 139913-94-3; (*Z*)-1-chloro-2-[*p*-(trifluoromethyl)phenyl]ethene, 139913-95-4; pyridine, 110-86-1; pyridinium (*p*-trifluoromethyl)benzylide, 139913-97-6; tetramethylethene, 563-79-1; 1-chloro-1-[*p*-(trifluoromethyl)benzyl]-2,2,3,3-tetramethylcyclopropane, 139913-98-7; chloro(*p*-chlorobenzyl)carbene, 88211-10-3; pyridinium *p*-chlorobenzylidide, 139913-99-8.

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Evidence for Ground-State s-cis Conformers in the Fluorescence Spectra of *all-trans*-1,6-Diphenyl-1,3,5-hexatriene

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Abstract: The temperature and excitation wavelength dependencies of the fluorescence spectrum of *all-trans*-1,6-diphenyl-1,3,5-hexatriene were studied in methylcyclohexane. As previously reported, the increase in *T* leads to relatively enhanced emission at the onset and tail portions of the fluorescence spectrum. Enhanced emission at the tail portion of the fluorescence spectrum is also observed at constant *T* by moving to longer excitation wavelengths. The results are consistent with thermal repopulation of the 1^1B_u state leading to enhanced onset emission and with population of excited s-cis conformers of the triene either by increasing their ground-state concentration (higher *T*) or by selective excitation (longer λ_{exc}) leading to enhanced tail emission. Application of principal-component analysis with self-modeling to matrices composed of fluorescence spectra for different λ_{exc} and constant *T* (30.0 or 91.0 °C) allows their resolution into two components, one of which is the combined $2^1\text{A}_\text{g}/1^1\text{B}_\text{u}$ fluorescence from the all-s-trans conformer and the other of which is an emission spectrum that we assign to s-cis conformers. The fractional contribution of s-cis conformer fluorescence in observed spectra for $\lambda_{\text{exc}} = 355$ nm increases from 6 to 25% as *T* is increased from −3.2 to +91.0 °C and is significantly higher at longer λ_{exc}, leading to an estimated enthalpy difference for conformer equilibration of 3.4 ± 0.4 kcal/mol.

Several reviews of polyene spectroscopy are available.[1-4] Numerous experimental[5-10] and theoretical[11-15] investigations have confirmed Hudson and Kohler's assignment of the fluorescence spectrum of *all-trans*-1,8-diphenyl-1,3,5,7-octatetraene to the $2^1\text{A}_\text{g} \rightarrow 1^1\text{A}_\text{g}$ transition, and spectroscopic evidence similarly supports the 2^1A_g assignment to the lowest excited singlet state of *all-trans*-1,6-diphenyl-1,3,5-hexatriene, DPH (Figure 1). The $2^1\text{A}_\text{g} \leftarrow 1^1\text{A}_\text{g}$ transition is symmetry forbidden in the single-photon absorption spectrum and allowed in the two-photon absorption (fluorescence excitation) spectrum; the converse applies for the $1^1\text{B}_\text{u} \leftarrow 1^1\text{A}_\text{g}$ transition. Effective experimental radiative rate constants, $k_\text{f}^{\text{obsd}} = \phi_\text{f}^{\text{obsd}}/\tau_\text{f}^{\text{obsd}}$, for DPH and higher polyenes are much smaller than calculated theoretical radiative rate constants, k_f^{th},[18,19] in agreement with assignments of k_f^{obsd} and k_f^{th} to k_{fa} and

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