($\Phi_{\text{sensitization}}$) remains relatively constant, while the quantum yields for the formation of **2** increase by a factor of 9 as one progresses from **4** to **9** and **10** as sensitizer. Quenching rate constants (k_q, $M^{-1}\ s^{-1}$) for **4**, **7**, **8**, and **9** were 1.66×10^{10}, 1.06×10^{10}, 1.09×10^{10}, and 9.8×10^9, respectively, for the quenching of sensitizer fluorescence by **1** in acetonitrile.[18] Thus, electron transfer from the substrate, **1** [$E_{1/2}$(ox) = 1.77 V], to the excited-state oxidant would appear to be diffusion controlled. This indicates that there is little, if any, observable steric hindrance to the initial electron transfer from **1** to the excited-state oxidant. Thus, the major influence of the bulky substituents must be on back electron transfer. This is consistent with the hypothesis that back electron transfers are "very sensitive to small structural changes."[19,20]

In summary, we have demonstrated the advantages which can accrue through the use of sterically encumbered sensitizers in photoinduced SET reactions.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

Registry No. **1**, 5636-65-7; **2**, 38624-29-2; **3**, 22616-89-3; **4**, 623-26-7; **5**, 1591-30-6; **6**, 137396-51-1; **7**, 86-53-3; **8**, 2619-37-6; **9**, 137396-52-2; **10**, 137396-53-3; dihydro-5-[1-(4-cyanophenyl)-1-methylethyl]-2(3*H*)-furanone, 137396-54-4.

Supplementary Material Available: Properties of the sensitizers **4**–**10** including UV absorption, fluorescence emission, quantum yield for fluorescence, and ground-state reduction potentials (1 page). Ordering information is given on any current masthead page.

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(18) The excited-state lifetimes of **4**, **7**, **8**, and **9** were 9.70,[5] 8.92,[9] 7.22, and 6.53 ns, respectively. We thank Dr. K. Tominaga for measuring the lifetimes of **8** and **9**.

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(20) The role of biphenyl in these reactions is not completely evident. In the absence of biphenyl, reaction times increase dramatically, although overall yields decrease only slightly.

Spectroscopic Detection of Ammonium Ylides from Arylchlorocarbenes and Amines

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The reactions of carbenes with amines have been extensively studied[1-4] and the subject has been recently reviewed.[5] In most cases an ammonium ylide is invoked as an intermediate for this reaction. The spectroscopic detection of this intermediate has only been reported for the reaction of 1-naphthylcarbene and triethylamine,[6] and the role of an ammonium ylide in the mechanism of carbene insertion into the N–H bond of amines has never been demonstrated. Laser flash photolysis (LFP) of 3-chloro-3-aryldiazirines in the presence of diethylamine (DEA) make possible direct observation of the UV spectrum of ammonium ylide, and therefore the formal insertion into N–H bonds is classified as a two-step process.

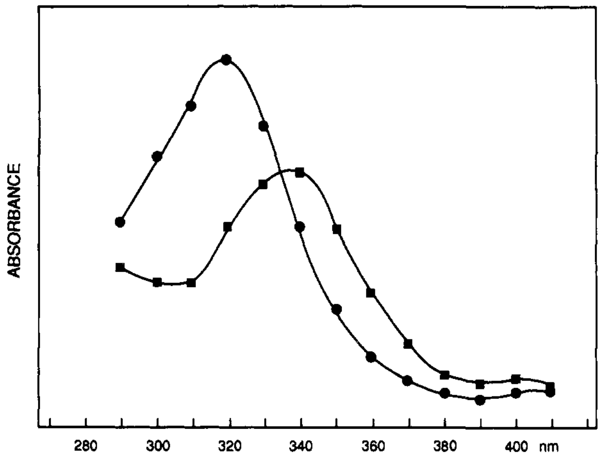

Figure 1. Transient absorption spectra for a solution of 3-chloro-3-(*p*-chlorophenyl)diazirine (0.015 M) and DEA (0.048 M) in isooctane. Time (t) after 200-ps excitation at 355 nm is (●) 0 and (■) 16 ns.

Photolysis of 3-chloro-3-aryldiazirines in the presence of DEA yielded *N,N,N′,N′*-tetraethylbenzylidenediamines as observed by Tomioka et al.[7] These authors suggested that the free arylchlorocarbene reacts with the N–H bond of the amine to afford the α-chlorobenzylamine which should easily undergo attack by a second DEA to give the final product. 3-Chloro-3-(*p*-chlorophenyl)diazirine (PCPD) (10^{-2} M) in isooctane was flashed with a 200-ps, 355-nm pulse from a frequency tripled mode-locked Nd-YAG laser. The quenching rate constant of the carbene **1**, p-Cl-Ph$\ddot{\text{C}}$Cl, monitored at 310 nm, by DEA was obtained in the usual manner by plotting the observed pseudo-first-order rate constant ($k_{\text{obs}} = k_0 + k_q$[amine] where k_0 is the rate constant of carbene decay in the absence of quencher) for the carbene decay vs [DEA] from 0.5–10 mM. The linear plot yielded a rate constant for the reaction of **1** with DEA at 27 °C of $k_q(\mathbf{1}, \text{DEA}) = (2.33 \pm 0.10) \times 10^9\ M^{-1}\ s^{-1}$.

For DEA concentrations less than 10 mM, no new transient other than that of the carbene was detected.[8] When the DEA concentrations are sufficiently high (20–400 mM), an additional transient ($\lambda_{\max}$ = 340 nm) was observed (Figure 1). It can easily be seen from this figure that during the first 16 ns after excitation there is a growth of a new transient in the 340–400-nm region. We attribute this transient to the absorption of the ammonium ylide because (1) this transient is absent in the absence of DEA and (2) its rate of growth matches the rate of decay of the carbene as extrapolated from data at low [DEA]. These results are given in a log–log plot of k_{obs} vs [DEA]. In the 20–400-mM DEA range, k_{obs} vs [DEA] deviates from linearity which can be explained by the increasing contribution of ylide absorption to the measured signal. At low [DEA], a slope of unity is obtained in agreement with $k_{\text{obs}} = k_0 + k_q[\text{amine}] \simeq k_q[\text{amine}]$, which leads to $\log k_{\text{obs}} = \log k_q + \log[\text{amine}]$, whereas at high [DEA], the slope is not unity but not zero. The spectrum of the ylide was made at [DEA] = 4.8×10^{-2} M which is indicated by point A in Figure 2. A lifetime around 26 ns at point A was obtained by a first-order analysis of the decay of the transient absorption at 310 nm. In fact, this absorption is the sum of the carbene and the ylide absorptions so that the decay is not simply first order. The carbene lifetime extrapolated from data at low [DEA] is 9 ns. Also, if a first-order analysis is performed at 360–380 nm, where carbene absorption is low compared to that of the ylide, the decay time of the ylide is 32 ns. Figure 3 shows the analysis of the transient absorption at 340 nm as the sum of the absorptions of the carbene and of the ylide with lifetime of 10 and 32 ns, respectively. The

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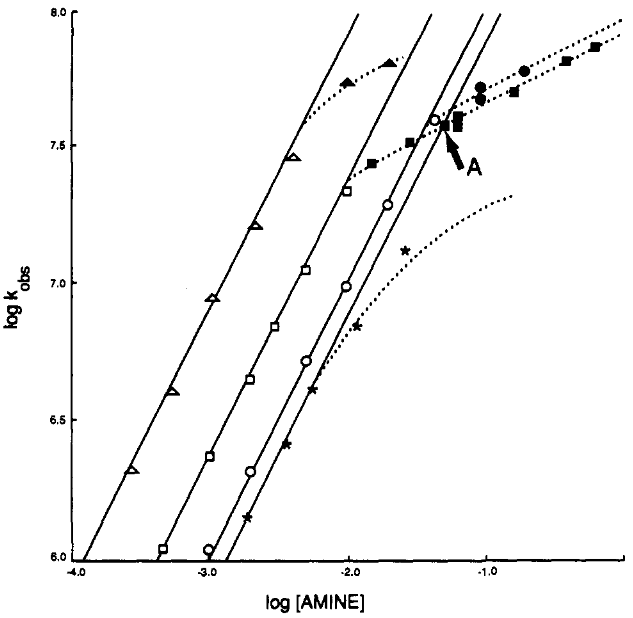


Figure 2. Plots for log k_{obs} vs log [amine]: (△) PCPD + *N*-methylaniline (monitored at λ = 310 nm); (▲) PCPD + *N*-methylaniline (λ = 400 nm); (□) PCPD + diethylamine (λ = 310 nm); (■) PCPD + diethylamine (λ = 340 nm); (○) PMPD + diethylamine (λ = 310 nm); (●) PMPD + diethylamine (λ = 340 nm); and (*) PCPD + triethylamine (λ = 310 nm).

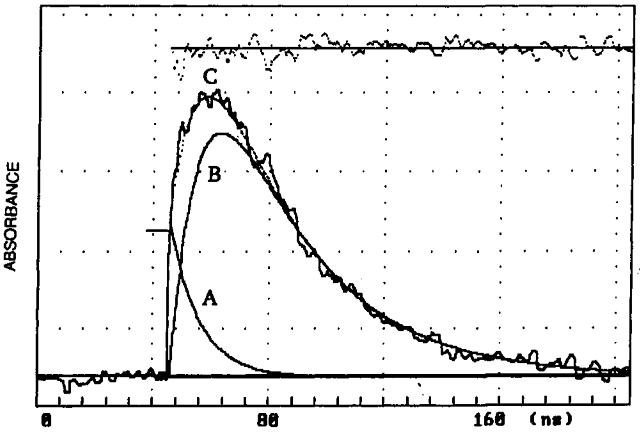
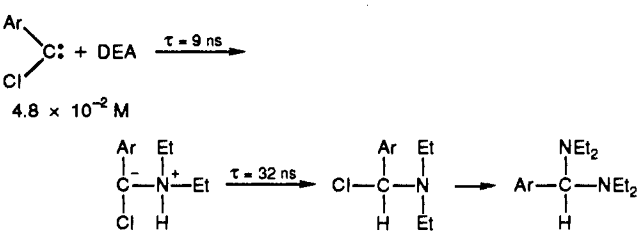


Figure 3. Analysis of the transient absorption at 340 nm for a solution of 3-chloro-3-(*p*-chlorophenyl)diazirine (0.015 M) and DEA (0.048 M) in isooctane (excitation 355 nm, 200 ps; temperature 27 °C): (A) decay of the *p*-chlorophenylchlorocarbene: 10 ns lifetime (B) growth and decay of the ylide with 10 and 32 ns growth and decay times; and (C) experimental data fitted with the sum of the theoretical curves A and B.

rapid disappearance of the ylide with $k = 3.1 \times 10^7\ s^{-1}$ (1/32 ns) is attributed to the 1,2 proton transfer in the ammonium ylide.



At high [DEA], the lifetime of the ylide measured at 340 nm (■ in Figure 2) decreases as [DEA] increases. This indicates that the proton transfer in the ylide is base catalzyed. Similarly, LFP of 3-chloro-3-(*p*-methylphenyl)diazirine (PMPD) in isooctane yielded *p*-CH_3-PhC̈Cl (**2**). The quenching of carbene **2**, monitored at 310 nm, at 27 °C yielded very similar results with $k_q(\mathbf{2}, \mathrm{DEA}) = 1.08 \times 10^9\ M^{-1}\ s^{-1}$ for [DEA] = 1–40 mM and a minimum [DEA] around 40 mM to get a detectable ylide absorption, and a similar lifetime for the ylide i.e. similar rate constant for the 1,2 proton transfer. The spectrum of this ylide is similar to the one given in Figure 1 except that the λ_{max} is blue shifted by 10 nm.

The difference in the reactivities of carbenes **1** and **2** is clearly due to the electronic effect of the para substituent. Since, in the ylide, the carbene is the electron-accepting species, any substituent which increases the electron density on the carbene center will decrease the reactivity.

Behavior of carbene **1** with tertiary (triethylamine, TEA) and aromatic (*N*-methylaniline, MAN) amines was examined. The quenching of carbene **1** by these amines at low concentrations gave the following rate constants: $k_q(\mathbf{1}, \mathrm{TEA}) = 7.2 \times 10^8\ M^{-1}\ s^{-1}$ and $k_q(\mathbf{1}, \mathrm{MAN}) = 8.0 \times 10^9\ M^{-1}\ s^{-1}$.

In the case of TEA, the ylide lifetime is an order of magnitude longer than for DEA, but the lack of a clear absorption spectrum makes an exact determination difficult. Further experiment will examine the reaction of arylchlorocarbenes with other amines.

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Tandem Diels–Alder/Double Intramolecular Two-Alkyne Annulations of Fischer Carbene Complexes: A One-Pot Construction of All Four Rings of the Steroid Ring System

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All of the reported syntheses that have employed annulations of Fischer carbene complexes[1] produce benzene rings in a process that incorporates the carbene carbon and 1 equiv of the alkyne.[2,3] Analogous annulations that incorporate the carbene ligand and 2 equiv of the alkyne have not been employed in synthesis.[4-7] We report here the first examples of double intramolecular two-alkyne

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