FMOC-Cl[7] in 5 mL of CH_2Cl_2 added via cannula with stirring. After 10 min at -30 °C and 30 min at 0 °C the precipitate was filtered, washed with MeOH, and dried in vacuo to give 311 mg (73%) of the hydrazide as a white powder, mp 163 °C dec. The analytical sample was prepared by briefly warming a suspension in acetone, filtering, and cooling at -20 °C to give a white solid: mp 165 °C dec; IR (Nujol) 1692 cm^{-1} (C=O); ^1H NMR (DMSO-d_6, 300 MHz) δ 4.15 (s, 2, aziridine CH), 4.23 (t, 1, fluorene 9-H), 4.36 (d, 2, CH_2), 7.2–8.0 (m, 14, aryl), 9.22 (br s, 1, NH). Anal. Calcd for $C_{27}H_{20}N_2O_2$: C, 80.16; H, 4.99; N, 6.93. Found: C, 80.23; H, 5.01; N, 6.82.

***N*-(Benzoylamino)acenaphthyleneimine (22b).** A solution of 460 mg of *N*-aminoacenaphthyleneimine in 15 mL of dry THF was cooled to -50 °C, and with stirring over 2 min a solution of 570 mg of benzoic anhydride in 3 mL of ether was added via cannula. After 5 min at -50 °C the mixture was warmed to 0 °C over 30 min, and the precipitate was filtered, washed with both ether and MeOH, and dried in vacuo to give 517 mg (72%) of the hydrazide as a white powder, mp 126 °C dec. The analytical sample was prepared as given for the FMOC analogue: mp 130 °C dec; IR (Nujol) 1639 cm^{-1} (C=O); ^1H NMR (DMSO-d_6, 300 MHz) δ 4.35 (s, 2, aziridine CH), 7.4–7.85 (m, H, aryl), 10.3 (br s, 1, NH). Anal. Calcd for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N, 9.79. Found: C, 79.52; H, 4.68; N, 9.79.

***meso*-Hydrobenzoin Dimesylate.** To a solution of 30 g of *meso*-hydrobenzoin[27] in 600 mL of dry pyridine there was added 64.5 mL of methanesulfonyl chloride over a period of 10 min with stirring and cooling in an ice bath. After 30 min, 18 mL of H_2O was added, stirring was continued for 2 h, and the mixture was poured into 1000 mL of $CHCl_3$; the resulting suspension filtered and washed twice each with H_2O, acetone, and ether. Recrystallization from acetone gave 26.8 g (52.5%) of the sulfonate as white crystals, mp 120 °C dec; IR (Nujol) 1355, 1180 cm^{-1} (SO_2). Anal. Calcd for $C_{16}H_{18}O_6S_2$: C, 51.87; H. 4.90; O, 25.92. Found: C, 52.05; H, 4.95; O, 25.90.

1-Amino-*cis*-2,3-diphenylaziridine. A suspension of 4.0 g of *meso*-hydrobenzoin dimesylate in 75 mL of 95% hydrazine was heated with stirring under N_2 to an internal temperature of 60–65 °C (optimum temperature 62 °C) for 24 h. Hexane (200 mL) was added, stirring was continued for 30 min, the hexane was decanted, and the residue was extracted with three 50-mL portions of hexane. The combined hexane extracts were dried over $MgSO_4$, the solvent was removed in vacuo, and the residue was recrystallized from hexane to give 0.8–1.02 g (35–45%) of the aminoaziridine as white crystals, mp 100–104 °C. The analytical sample (pentane) had mp 110–111 °C: ^1H NMR ($CDCl_3$) δ 3.14 (s, 2, CH), 3.8 (br s, 2, NH), 7.12 (s, 10, aryl). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.33. Found: C, 80.03; H, 6.81; N, 13.23.

1-Phthalimido-*cis*-2,3-diphenylaziridine. A solution of 0.22 g of **25** dissolved in 10 mL of CH_2Cl_2 was treated with 0.23 g of *N*-carbethoxyphthalimide.[16] After the mixture was stirred at room temperature for 1 h, evaporation in vacuo gave a white residue, which was washed with ether and recrystallized from EtOAc–Et_2O to give 0.3 g (67%) of phthalhydrazide **26** as colorless needles. The crude product [Anal. Calcd for $C_{25}H_{23}N_3O_4$: C, 69.93; H, 5.36. Found: C, 70.40; H, 5.58] was refluxed in ethanol for 2 h, the mixture was evaporated in vacuo, and the residue was washed with Et_2O and recrystallized from hexane–Et_2O to give 0.15 g of the phthalimido derivative **27** as pale yellow needles, mp 125–126 °C, identified by mixture melting point and comparison of IR and ^1H NMR spectra with the sample obtained[6] by oxidation of *N*-aminophthalimide by $Pb(OAc)_4$ in the presence of *cis*-stilbene.

Thermolysis of *N*-[[[(9-Fluorenylmethyl)oxy]carbonyl]amino]acenaphthyleneimine in Cyclohexene/Benzene. A suspension of 198 mg of hydrazide **22a** in 20 mL of cyclohexene/benzene (1:1) was stirred under N_2 at 60 °C for 16 h. The solid eventually dissolved. Removal of solvent gave a residue, which by flash chromatography on silica gel with elution by hexane gave a yellow material, which was rechromatographed in the same way to give 66.5 mg (89%) of acenaphthylene, mp 88–92 °C, identified by IR and ^1H NMR spectral comparison. Switching to elution by 10% ether in CH_2Cl_2 gave 91.1 mg of material, which was rechromatographed with 40% EtOAc in hexane to give 75.0 mg (46%) of cyclohexyl hydrazide **7a** as a fluffy white solid, mp 161–165 °C dec, identified on the basis of IR and ^1H NMR spectral comparison with an authentic sample (see above). Only traces of *N,N'*-bis(FMOC)hydrazine were detected in the reaction mixture by TLC analysis.

Thermolysis of *N*-(Benzoylamino)acenaphtheneimine in Cyclohexene/Benzene. A suspension of 288 mg of hydrazide **22b** in 20 mL of cyclohexene/benzene (1:1) was stirred under N_2 at 55–60 °C for 7 h. Complete solution never occurred. The suspension was cooled and filtered to give 39.5 mg (33%) of 1,2-dibenzoylhydrazine, mp 241–243 °C (lit.[20] mp 241 °C), identified by IR spectral comparison with an authentic sample. Flash chromatography as described for the analogous FMOC derivative gave 131.7 mg (86%) of acenaphthylene, mp 91–93 °C, and 17.5 mg (8%) of cyclohexylhydrazide **7b**, mp 147–151 °C, identified by comparison with an authentic sample prepared by benzoylation of the corresponding free aminoaziridine (see above). For thermolyses of other compounds, see Table II.

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The Unusual Reactivity of 9,9'-Dianthrylcarbene[1]

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9,9'-Dianthrylcarbene was investigated by using laser flash photolysis, conventional flash photolysis, and optical modulation spectroscopy. Its optical absorption spectrum was characterized by two strong bands at 355 nm (ϵ 3.9 × 10^4 M^{-1} cm^{-1}) and at 445 nm (ϵ 2.9 × 10^4 M^{-1} cm^{-1}). Although the carbene has a triplet ground state, the rate constant for its spin-allowed reaction with oxygen was ca. 5 × 10^5 M^{-1} s^{-1}, yet it underwent self-reaction at the diffusion-controlled limit. These unusual kinetic properties stem from the fact that the carbene has a structure in which the unpaired electrons are highly delocalized.

There has been a great deal of theoretical[2-4] and experimental[5-11] interest in the way that carbene structures affect the energy separation between the triplet and singlet electronic states. We have recently shown that increasing

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the central C–C–C angle in diarylcarbenes has the affect of increasing this energy separation. Theory suggests that the angular expansion causes a slight stabilization of the triplet state and a dramatic destabilization of the singlet.[3]

Diphenylcarbene is the prototypical diarylcarbene. It has a central C–C–C angle of 148° and a dihedral angle of 35° between the phenyl rings.[5-8] The triplet ground state of this carbene displays many of the chemical properties normally associated with the singlet state, e.g. it inserts into the O–H bonds of alcohols and the N–H bonds of amines. The mechanisms by which these reactions take place have been disputed. One school of thought suggests that the triplet carbene and the singlet are in thermodynamic equilibrium so that the triplet functions as a reservoir for the highly reactive singlet state.[10,11] On the basis of kinetic evidence, we favor a direct reaction between the triplet carbene and substrates that have singlet ground states, arguing that intersystem crossing to singlet product takes place during this process.[9] Whichever mechanism applies, it is clear that the triplet and singlet states of diphenylcarbene must be close so that either a thermodynamic equilibrium or an intersystem crossing process allows the triplet to manifest singletlike chemistry.

Small changes to the central C–C–C angle in carbenes can be achieved by the introduction of groups that cause steric crowding. However, they have a profound effect on the chemistry of the carbenes concerned. For example, dimesitylcarbene has a larger central C–C–C angle than diphenylcarbene, and its singlet and triplet states display quite distinct chemistries.[9a] There is no evidence that the triplet dimesitylcarbene can access the singlet manifold to produce the singletlike reactions that are observed for diphenylcarbene.

The deviation from axial symmetry in triplet carbenes or, roughly speaking, the degree of bending is reflected by the zero field splitting parameter, E, weighted by D, which is inversely proportional to the cube of the distance between the electrons. Both of these parameters can be measured by using electron paramagnetic resonance (EPR) spectroscopy. In diphenylcarbene the ratio E/D is 0.0467 while for dimesitylcarbene the value is 0.0421.[9c] While the difference is fairly small, the triplet and singlet states of these carbenes exhibit quite different chemistries. The sensitivity of the relationship between chemistry and structure is underscored by triplet fluorenylidene where $E/D = 0.0694$[7] and where it is virtually impossible to disentangle the chemistries of the singlet and triplet states because the energy separation between the states is extremely small.[9d,11b]

In this context, 9,9′-dianthrylcarbene, I, represents an extreme case. When formed in matrices of its parent diazo compound, eq 1, it shows relatively small values for both E and D.[12] This means that its structure is close to linear

$$(\mathrm{An})_2\mathrm{CN}_2 \xrightarrow{h\nu} \underset{\mathrm{I}}{(\mathrm{An})_2\mathrm{C}:} + \mathrm{N}_2 \qquad (1)$$

An = 9-anthryl

and that there is a large separation between the unpaired electrons, implying that the carbene has a substantial degree of allenic character. Annealing the matrix allows the carbene to adopt its minimum energy structure, which is completely linear, i.e. the value of E has dropped to zero.

The spectroscopic results suggest that 9,9′-dianthrylcarbene ought to display chemistry that is substantially different than that observed for other diarylcarbenes. In this work we describe a series of kinetic and product studies on the reactions of 9,9′-dianthrylcarbene. The results vindicate this expectation and provide some interesting insights into structure–reactivity relationships of diarylcarbenes.

Experimental Section

Materials. Dianthryldiazomethane was prepared by the method described by Greene and his co-workers.[12,13] Benzene was purified by distillation from sodium prior to use. Acetonitrile was stirred with a mixture of potassium carbonate and potassium permanganate (16 h), filtered, distilled, and finally fractionally distilled from calcium hydride. Other solvents were spectroscopic grade and were used without further purification.

Laser Flash Photolysis. The laser flash photolysis technique has been described in detail elsewhere.[14] Briefly, samples were irradiated with pulses from a nitrogen laser (337.1 nm, 8 ns duration, up to 10 mJ power) or an excimer laser (308 nm, 4 ns duration, up to 80 mJ power). The transients thus generated were monitored with a detection system consisting of a low-powered xenon lamp and a monochromator fitted with a photomultiplier tube detector. Signals from the photomultiplier were digitized (Tektronix 7912) and were then transferred to a PDP 11/23 computer for storage and analysis.

In a typical experiment, solutions of the dianthryldiazomethane (ca. 1×10^{-4} M) in a given solvent were deoxygenated by nitrogen purging for 30 min. The solutions were then flowed through an optical cell (7 × 7 mm) at a rate such that the sample volume irradiated was replenished between each laser pulse.

Conventional Flash Photolysis. Samples were prepared as described above and flowed through an optical cell (10 cm × 1 cm diameter) inside a PRA Model FP-1000 conventional flash photolysis apparatus. Kinetic traces were recorded on a Tektronix 2230 digitizer and were then transferred to a computer for storage and analysis.

Optical Modulation Spectroscopy. A detailed description of the apparatus is given elsewhere.[15] Samples were deoxygenated as described above and irradiated in a quartz flow cell (Starna 43Q, 4 mm path length) with a 1000-W mercury–xenon lamp (Hanovia 997B001). The light from the lamp was modulated with a mechanical chopper fitted with irises so that the light intensity at the sample rose and fell as a sine wave. Consequently, the concentration of the transient generated was modulated sinusoidally.

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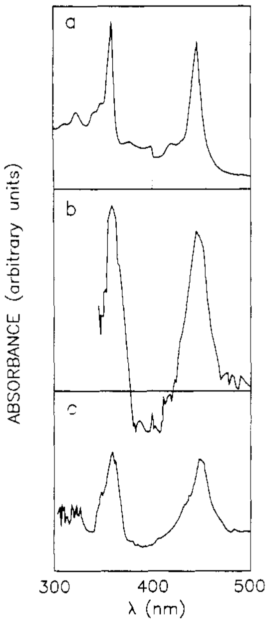

Figure 1. Absorption spectrum of 9,9′-dianthrylcarbene, I, generated by photolysis of the diazo compound (1.0×10^{-4} M) by using (a) matrix isolation, 77 K (isopentane/ether), (b) laser flash photolysis, 298 K (benzene), and (c) optical modulation spectroscopy, 298 K (acetonitrile).

The transients were detected by using an optical system arranged at right angles to the photolysis direction, which was similar to that used for laser flash photolysis. In this case, the output from the photomultiplier tube was sent to a lock-in amplifier (PAR 124A), which was used to detect the very small AC signal due to the modulated absorption of the transient. Spectra were obtained by monitoring the optical density due to the transient as a function of wavelength, and kinetic data were obtained by monitoring the phase-angle dependence of the transient signal as a function of the modulation frequency.

Matrix Isolation. Solutions of 9,9′-dianthryldiazomethane (ca. 0.1 mM) in isopentane/ether were degassed by using several freeze–pump–thaw cycles and were sealed into quartz EPR tubes. The solutions formed transparent glasses when cooled to 77 K. Photolysis of these frozen solutions gave the matrix isolated carbene which was monitored with either a Varian E104 EPR spectrometer or a Hewlett-Packard 8450A UV–visible spectrophotometer.

Other Instrumentation. NMR spectra were obtained with a Bruker WP80 instrument. Mass spectra were measured on a VG Analytical 7070E mass spectrometer at the University of Ottawa Mass Spectrometry Centre (we thank Drs. J. Krause and C. Kazakoff for their help with these experiments).

Product Studies. Product studies were carried out under various conditions. For example, the diazo compound (9.8 mg, 2.5×10^{-5} mol) was dissolved in 250 mL of benzene in a Pyrex flask, and the solution was purged with argon for 30 min. In some cases, methanol, 25 mL, was then added, and purging was continued for an additional 30 min. The solution was then irradiated with either a 150-W "sun lamp" or at 350 nm in a Rayonet Reactor. The solvent was removed on a rotary evaporator, and the products were analyzed by preparative thin-layer chromatography.

The products obtained both in the presence and absence of methanol were 9,9′-dianthryl ketone (45%) and anthraquinone (45%), which were identified by comparison with authentic samples.

Results and Discussion

Matrix Isolation. Brief photolysis of a glass at 77 K containing 9,9′-dianthryldiazomethane (0.1 mM) with a UV lamp led to a persistent optical signal with two well-defined bands at 355 and 445 nm (Figure 1a). However, no EPR spectrum was observed when the same sample was placed inside the spectrometer cavity. Further irradiation led to the appearance of a EPR spectrum that was identical with that previously reported for 9,9′-dianthrylcarbene,[12] but the two optical absorption bands in the sample were then so intense (OD > 2) that the UV–visible spectrum could no longer be properly recorded. Warming and softening the matrix led to the destruction of both signals. However, it was shown qualitatively, by monitoring the shoulders of the absorption bands, that the two persistent optical signals increased in intensity with the growth of the EPR spectrum, and so we tentatively assigned the bands as being due to the triplet carbene.

Laser Flash Photolysis. The transient optical absorption spectrum obtained in solution at 298 K by using laser flash photolysis (Figure 1b) was identical with that observed in the matrix. Furthermore, the spectrum, although red-shifted, was similar to that of the structurally related di-9-anthrylmethyl radical (λ_{max} 340 and 430 nm).[12]

This relationship seems to be quite general for diarylcarbenes and their corresponding diarylmethyl radicals.[16] Taken as a whole, the experimental evidence strongly supports the assignment of the optical absorption spectrum to I.

Direct photolysis of diaryldiazomethanes leads initially to singlet carbenes that, in most instances, undergo rapid intersystem crossing to the triplet ground states, eq 2, 3. The intersystem crossing process can be monitored with flash photolysis equipment with a picosecond response.[17] For example, singlet diphenylcarbene undergoes intersystem crossing with a rate constant of 3.2×10^9 s^{-1} in acetonitrile at 300 K.[17b]

$$Ar_2CN_2 \xrightarrow{h\nu} [Ar_2C:]^1 + N_2 \qquad (2)$$

$$[Ar_2C:]^1 \rightarrow [Ar_2C:]^3 \qquad (3)$$

Our instrument has a time resolution of 10 ns to 10 μs, and we are therefore unable to monitor the intersystem crossing process directly. However, in general it has been possible to set up a competition with intersystem crossing by chemically trapping the singlet carbene. For example, singlet diarylcarbenes can be readily intercepted by alcohols,[9b,10b] eq 4, and primary amines.[9e] These trapping

$$[Ar_2C:]^1 + ROH \rightarrow Ar_2CHOR \qquad (4)$$

reactions can be detected in our system since they lead to a reduction in the initial triplet concentration, and the kinetics for the reaction can be determined by the Stern–Volmer method.

For I the initial triplet concentration was unaffected by the addition of methanol. This was a surprising result in view of the fact that for all other carbenes where singlet to triplet intersystem crossing takes place, the singlet can be intercepted by using methanol as a scavenger. The reasons for this phenomenon are not clear. However, several explanations can be advanced to rationalize the observation.

First, the lifetime of singlet I may be far shorter than those of other diarylcarbenes. Second, typical reactions of singlet diarylcarbenes rely upon an electronic structure where the two nonbonded electrons form a lone pair and leave a vacant p orbital for substrate coordination (ylide formation). If, like its triplet, the singlet state of I has a linear structure, then the two nonbonded electrons with

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their antiparallel spins may be in separate, orthogonal orbitals. In essence, the lone pair/vacant orbital configuration that is required for alcohol scavenging may not be the lowest energy structure for this particular singlet. A third, and very simple alternative, is that the reactive center of the carbene is too well protected by the anthryl groups so that steric factors slow down the methanol reaction. However, it should be noted that steric interactions in dimesitylcarbene do not prevent methanol scavenging of its singlet state.[9a]

Of these various alternatives, the second seems to be the most attractive since it reflects the known tendency of I to adopt the linear structure that differentiates it from other diarylcarbenes. Clearly, this is an area where a theoretical approach could usefully be applied.

Once intersystem crossing had taken place, we were able to monitor the kinetic behavior of triplet I by using laser flash photolysis. Attenuating the laser pulses by using neutral density filters caused the initial concentration of triplet I to diminish. The reduction in concentration led to an increase in the lifetime of the carbene, suggesting that it was undergoing bimolecular self-reaction. This triplet–triplet processes is spin allowed, there being a 1/9 probability that the reaction of two triplet molecules can lead to a singlet product. However, the lifetime of the triplet carbene was unaffected when oxygen (1 atm) was used as a scavenger. Again this is a spin-allowed reaction and might reasonably have been expected to be more rapid than the biomolecular self-reaction of the sterically crowded carbene. We decided to persue this intruiging result by studying these reactions with techniques that operate on much longer time scales.

Conventional Flash Photolysis. By use of conventional flash photolysis, it was found that I decayed cleanly by second-order kinetics in nitrogen-purged solutions with a second-order rate constant, $2k_5/\epsilon = 2.3 \times 10^5$ cm^{-1} s^{-1} at 445 nm (eq 5). The decay kinetics were essentially unchanged when the experiment was repeated with an air-purged sample. Gas mixtures containing 40–80% oxygen (the remainder being nitrogen) gave signals that were very poorly defined, and it was impossible to distinguish between a first- or second-order process. Under the conditions of the experiment, however, it was possible to estimate an upper limit for the rate constant for reaction of I with O_2 of 1×10^6 M^{-1} s^{-1}.

$$\mathrm{I} + \mathrm{I} \rightarrow \text{products} \qquad (5)$$

Optical Modulation Spectroscopy. The absorption spectrum of I in acetonitrile was obtained by optical modulation spectroscopy (Figure 1c) and was identical with those found by using matrix isolation and laser flash photolysis. Under certain conditions, it is possible to obtain kinetic information by the modulation method and to determine extinction coefficients for the transient species in a way that completely eliminates actinometry.[18]

The technique uses modulated photolysis to cause the concentration of the transient to rise and fall as a sine wave. Phase-sensitive optical detection is then used to measure the optical density of the transient and its phase lag with respect to the photolyzing light. The lag is expressed in terms of the phase angle ϕ, and if there is no absorption by starting material or products at the monitoring wavelength, eq 6 applies where ω is the modulation frequency in rad s^{-1}. On the other hand, if regions exist where the starting material, transient, and products all absorb the monitoring light, the relationship between tan (ϕ) and τ is more complicated and depends on the extinction coefficients of all of the absorbing species (eq 7–10). In this case, the ratio of the extinction coefficients and τ can be treated as independent variables and can be fitted iteratively to the experimental frequency dependence of the phase angle.[19]

$$-\tan(\phi) = \omega\tau \text{ for } \omega\tau > 1 \qquad (6)$$

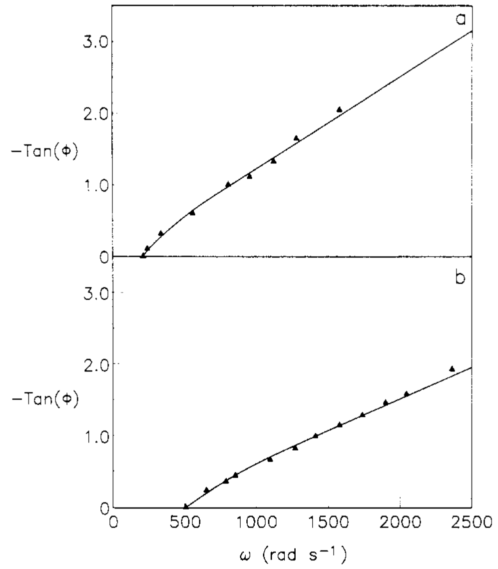

Figure 2. Plot of −tan (ϕ) vs modulation frequency (ω) used to measure the lifetime and extinction coefficients of I at (a) 355 nm and (b) 445 nm. The triangles are the experimental points. The line is the theoretical fit based on eq 7–10 (see the text for the values of the fitted parameters).

$$\tan(\phi) = \frac{\epsilon_S - \epsilon_P}{\epsilon_T - \epsilon_P} \cdot \frac{1}{F\tau\omega} - \left\{ f - \frac{\epsilon_S - \epsilon_P}{\epsilon_T - \epsilon_P} \cdot \frac{1}{F} \right\} \tau\omega \qquad (7)$$

where

$$F = g[(1 + \tau^2\omega^2)/(1 + f^2\tau^2\omega^2)]^{1/2} \qquad (8)$$

$$g = 1 + 0.2\exp(-2.67\tau\omega) \qquad (9)$$

$$f = 1 + \exp\{-3.08(\tau\omega)^{0.46}\} \qquad (10)$$

The results obtained for I in acetonitrile are illustrated in Figure 2. The lifetimes of the transient measured at 355 nm (1.4 ± 0.1 ms) and at 445 nm (1.1 ± 0.1 ms) are in reasonable agreement and give $(\epsilon_S - \epsilon_P)/(\epsilon_T - \epsilon_P) = 0.09 \pm 0.01$ and 0.25 ± 0.01 at the two respective wavelengths. The value of ϵ_T at each wavelength (ϵ_{355} 3.9×10^4 M^{-1} cm^{-1} and ϵ_{445} 2.9×10^4 M^{-1} cm^{-1}) was then simply determined from the known value of ϵ_S. At 355 nm it was also necessary to apply a correction for product absorption so that the uncertainty in that value is greater than at 445 nm. Combination of ϵ_{445} with the value of $2k_5/\epsilon$ gave an estimate of the rate constant for self-reaction of the carbene of 7×10^9 M^{-1} s^{-1}.

To ensure that the process being monitored was indeed the bimolecular self-reaction of the transient, we determined the kinetic order of the reaction by varying the modulated light intensity. For a first-order process no light intensity dependence of the transient lifetime is expected while for a second-order process the lifetime is expected to vary inversely as the square root of the light intensity (eq 11),[16] where I_0 is the rate of initiation. Analysis of the

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light intensity dependence of the lifetime of the carbene confirmed the flash photolysis result, i.e. the decay followed second-order kinetics.

$$\tau = (4k_5 I_0)^{-1/2} \qquad (11)$$

An independent estimate of $2k_5$ was possible by using eq 11, since the rate of initiation in this system could be estimated. This was done by measuring the flow rate of the sample through the optical cell and the conversion of the starting diazo compound by absorption spectrophotometry. By use of this method, I_0 was found to be ca. 5×10^{-5} M^{-1} s^{-1}, giving a value of $2k_5$ of ca. 8×10^9 M^{-1} s^{-1}, in good agreement with the value obtained in the flash photolysis experiment (vide supra).

When the solutions were oxygen purged, the absorptions due to the carbene completely disappeared. Based on this observation and the millisecond timescale of the modulation experiment, we estimated that the lower limit of the rate constant for the reaction of the carbene with oxygen must have been ca. 5×10^5 M^{-1} s^{-1}. This value is within a factor of 5–10 of the upper limit estimated from the flash photolysis experiments.

We were unable to detect the spectrum of the carbonyl oxide which is the expected product of this reaction, eq 12. However, this is hardly surprising since the carbonyl

$$\mathrm{An_2C}: + \mathrm{O_2} \rightarrow \mathrm{An_2C}{=}\overset{+}{\mathrm{O}}{-}\overset{-}{\mathrm{O}} \qquad (12)$$

oxide would, by analogy with benzophenone oxide, have a relatively weak absorption band at ca. 410 nm ($\epsilon \sim 1200$ M^{-1} cm^{-1})[20] and this would have been a factor of at least 50 weaker than the absorptions due to the carbene that were initially detected.

There is a striking contrast between the rate constant for the self-reaction of the carbene and that for its reaction with oxygen. Both are triplet–triplet processes and therefore have a 1/9 probability of being spin allowed. Yet the rate constant for the self-reaction is some 4 orders of magnitude larger than the reaction of the carbene with the smaller oxygen molecule.

The best rationale that we can offer for this observation is that the linear structure of the carbene has a high degree of allenic character so that a great deal of the spin density is delocalized onto the anthryl rings. Self-reaction between the two carbenes can therefore take place at the exposed 10 positions and will be relatively unhindered by steric effects. However, reaction of oxygen at this position to form a peroxy radical moiety is likely to be thermodynamically unfavorable[21] because of the high degree of stabilization associated with the anthryl system. This would mean that oxygen would need to attack the central carbon of the carbene to form the thermodynamically stable carbonyl oxide.[22] Since the central carbon is sterically protected and since the reaction with oxygen leads to a large change in geometry (and hybridization), the rate constant for the process might be expected to be fairly low.

Product studies on the anthryl system were not highly informative. However, the data that we were able to assemble are certainly consistent with the interpretation of the reaction kinetics. Photochemically initiated reactions of I (1×10^{-4} M) in benzene containing 0.5 M methanol gave only two products: 9,9′-dianthryl ketone and anthraquinone, each in 45% isolated yield. The failure to trap the carbene with methanol concurs with the kinetic experiments where the singlet carbene could not be intercepted by using methanol as a quencher. The formation of 9,9′-dianthryl ketone implies the intermediacy of the related carbonyl oxide since it is a product that is derived from carbonyl oxide self-reaction,[19] eq 12 and 13. While we are unable to be specific about the mechanism of formation of anthraquinone, we note that carbonyl oxides do rearrange to give products[23] that, in this case, might photolyze to produce anthraquinone.

$$2\mathrm{An_2C}{=}\overset{+}{\mathrm{O}}{-}\overset{-}{\mathrm{O}} \rightarrow 2\mathrm{An_2CO} + \mathrm{O_2} \qquad (13)$$

Reactions carried out at much higher concentrations (10^{-2} M) of diazo compound in carefully deoxygenated benzene gave an organic product that accounted for 50% of the mass balance. Under these conditions the rate of photolysis is at least 10 times greater than at 10^{-4} M diazo compound, and on the basis of the kinetic studies, we anticipated that the product might be the dimer of the carbene. However, we were unable to characterize its structure from its proton and carbon-13 NMR spectra. In addition, the material was too involatile for mass spectrometry and the crystals too poor for X-ray crystallography. The fate of the carbene in carefully degassed solvents can therefore only be inferred from the kinetics studies.

Summary

Dianthrylcarbene shows properties that are remarkably different from those of other diarylcarbenes. Its EPR spectrum, the failure of its singlet state to react with methanol, its rapid self-reaction, and its slowness to react with oxygen are all consistent with linear structures for its singlet and triplet states in which the bonding about the central carbon shows a high degree of allenic character.

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