= 9.3 eV, IP(CS_2) = 10 eV) and they serve as a nonreactive background for collisional stabilization. Samples were admitted to the mass spectrometer either by using a direct-insertion CI probe or through a custom-built heated inlet that was continually flushed with helium gas to aid in mass transfer and to eliminate electrical breakdown. Collision-induced dissociation was observed by admitting helium to the collision cell until a 50% reduction of the main beam was observed. The CAD spectra reported have not been corrected for unimolecular metastable contributions because these contribute less than 5% to any CAD signal, with the following exceptions: loss of C_6H_6 from 1-phenyltetralin, 12%; loss of C_6H_6 from 1,4-diphenylbut-1-ene, 17%; loss of CH_3 from *cis*-2,3-diphenylbut-2-ene, 8%.

Ionization and appearance energies were determined with a Kratos MS-50 mass spectrometer operated with the repeller voltage = 0 V and with a trap current of 36 μA. The IP and AP values were obtained by plotting log (I/I_0) vs. the ionizing voltage both for the unknown ion and for two reference ions. The reference ions that were used were C_6D_6, m/z 84 from deuterated benzene (IP = 9.25 eV) and 1,2,3,4-tetrahydronaphthalene, m/z 132 (IP = 8.44 eV).[27] The voltage corresponding to the onset of the unknown ion is calculated on the basis of the position of its curve relative to the curves of the reference ions (semilog method).

The rate constant was measured with a Varian ICR-9 spectrometer modified to operate in a trapped mode. An elongated cell similar to the type introduced by McIver was employed.[28] The spectrometer was operated at a magnetic field strength of 10.4 kG, 153.7-kHz excitation frequency, and an ionizing energy of 15 eV, as measured with a digital voltmeter. Styrene disappearance curves were recorded by monitoring m/z 104 intensity as ion detection delay time was increased from 0 to 500 ms under the control of a pulse programmer. Styrene pressure in the spectrometer was measured with an ion gauge. The ion gauge pressure values were corrected by calibrating the ion gauge against a Datametrics Model 1173 Barocel electronic manometer.

Materials. [2.2]Paracyclophane and stryene were purchased from Aldrich Chemical Co. The 1- and 2-phenyltetralins were synthesized by adding phenyllithium to 1- to 2-tetralone (Aldrich), respectively, and submitting the benzylic alcohols thus formed to a Birch reduction (Li/NH_3).[29] The *cis*-1,3-diphenylbut-1-ene was generously donated by C. A. Kingsbury and G. M. Underwood. The 1,4-diphenylbut-1-ene was synthesized by adding phenyllithium to 4-phenylbutanal and dehydrating the resulting alcohol by distillation in the presence of a catalytic amount of H_2SO_4. The 2,3-diphenyl-2-butene was made in a similar fashion from acetophenone and 1-phenylethyllithium.

cis- and *trans*-1,2-diphenylcyclobutane were synthesized according to the method of Dodson and Zielski.[30] cis-1,2-Diphenylcyclobutane-*1,2*-d_2 was obtained by hydrogenating 1,2-diphenylcyclobutene with D_2; the d_2 product was shown to be 10.5% d_0, 30.4% d_1, 51.9% d_2, and 7.2% d_3 by using mass spectrometry and low ionizing energy (10 eV).

1,4-Diphenylbutan-1-ol was obtained by reducing 4-phenylbutyrophenone (Aldrich) with lithium aluminum hydride in refluxing tetrahydrofuran. NMR 90 MHz ($CDCl_3$): δ 7.28–6.88 (complex, 10, aromatic), 4.60–4.41 (br t, 1, –CH), 2.66–2.38 (complex t, 2, –CH_2), 2.23 (br s, 1, –OH), 1.78–1.56 (complex, 4, –CH_2). Mass spectrum 70 eV (m/z, relative intensity): 226, 0.3%, 225, 0.2%; 224, 0.2%; 210, 0.9%; 209, 1.4%, 208, 4.6%; 133, 0.6%; 131, 0.7%; 130, 0.5%; 129, 0.8%; 121, 1.3%; 120, 10.2%; 118, 2.0%; 117, 12.1%; 116, 1.3%; 115, 5.1%; 108, 5.2%; 107, 67.1% 106, 1.5%; 105, 19.7%, 104, 100%; 103, 3.4%; 92, 5.4%; 91, 7.3%; 89, 1.5%; 80, 3.1%; 79, 43.3%; 78, 8.0%; 77, 23.8%; 65, 7.4%; 63, 1.6%; 53, 1.0%; 52, 1.6%; 51, 6.3%.

1,4-Diphenylbutan-1-ol-*4,4*-d_2 was synthesized starting from 4-phenylbutyric-*4,4*-d_2 acid,[19a] which was reduced to 4-phenylbutan-1-ol-*4,4*-d_2 with lithium aluminum hydride. The alcohol was then oxidized to 4-phenylbutanal-*4,4*-d_2 with pyridinium chlorochromate.[31] The 4-phenylbutanal-*4,4*-d_2 was reacted with a 10% molar excess of phenylmagnesium bromide according to standard procedures.[32] The crude product was chromatographed on silica gel with a 10% ethyl acetate/petroleum ether eluant solution. The product was purified by sublimation at 10 mtorr, 55 °C. The NMR and mass spectral analysis were consistent with 1,4-diphenyl-butan-1-ol-*4,4*-d_2. Elemental composition was determined by mass spectrometry at low ionizing energy (10 eV) to be 85.4% d_2, 15.6% d_1.

Water Elimination from 1,4-Diphenylbutan-1-ol-*4,4*-d_2. Mass spectrometry was used to measure the D/H distribution in the products of ionic water elimination, and the following products were obtained: –H_2O, 15.1%; –DOH, 77.0%; –D_2O, 7.9%. The combination of unknown isotope effects and possible competing mechanisms makes the exact assignment of mechanism and k_H/k_D value impossible. However, a regiospecificity of 99.3% was calculated by using a k_H/k_D of 2.20.[33] The most mechanistically mixed possibility would be calculated for k_H/k_D = 1.0, which yields 92.2% regiospecificity. Therefore, contributions from elimination mechanisms other than 1,4 account for at most 7.8% of the total water loss and are likely <1% of the total.

Registry No. Styrene radical cation, 34504-74-0; styrene, 100-42-5; styrene ion-molecule adduct, 74168-41-5; *cis*-1,2-diphenylcyclobutane radical cation, 88243-92-9; *trans*-1,2-diphenylcyclobutane radical cation, 88243-93-0; [1,4-diphenylbutan-1-ol-H_2O] radical cation, 71364-17-5; [2.2]paracyclophane radical cation, 88243-94-1; 2-phenyltetralin radical cation, 88181-24-2; 1-phenyltetralin radical cation, 88181-25-3; 1,4-diphenylbut-1-ene radical cation, 88243-95-2; 1,3-diphenylbut-1-ene radical cation, 88243-96-3; *cis*-2,3-diphenylbut-2-ene radical cation, 85549-56-0; *cis*-1,2-diphenylcyclobutane-*1,2*-d_2 radical cation, 88181-26-4; 1,4-diphenylbutan-1-ol-*4,4*-d_2, 88181-27-5.

Singlet and Triplet Dimesitylcarbene[1]

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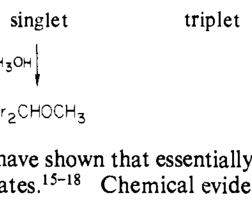
Abstract: The triplet states of essentially all diarylcarbenes react with substrates such as methanol or their parent diazo compounds both of which are thought to be specific quenchers for the singlet state. To rationalize these results, investigators have proposed that the singlet and triplet states of these carbenes are linked by efficient equilibria. In this kinetic study we have found that the singlet and triplet states of dimesitylcarbene exhibit quite distinct chemistries. The singlet state alone reacts with methanol, 1-propanol, and 1,3-cyclohexadiene, while the triplet carbene dimerizes to give olefin or, for example, reacts with oxygen. No evidence was found for reaction of the triplet carbene via the singlet manifold. Arguments are presented to explain the enhanced free energy difference between the spin states of this carbene and the relative persistence of its triplet.

The relationship between singlet and triplet states in diarylcarbenes has attracted the interest of many investigators.[2-14]

Scheme 1



Spectroscopic studies have shown that essentially all such carbenes have triplet ground states.[15-18] Chemical evidence has led to the

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(1) Issued as NRCC publication No. 22629.

(2) (a) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1964. Jones, M., Jr.; Moss, R. A. "Carbenes"; Wiley: New York, 1973. (b) Etter, R. M.; Skovronek, H. S.; Skell, P. S. *J. Am. Chem. Soc.* **1959**, *81*, 1008. For further examples see ref 3–14.

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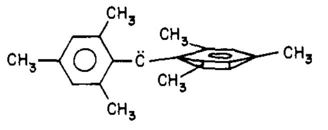
0002-7863/84/1506-0543$01.50/0

conclusion that the singlet state can be intercepted and that it displays different chemistry from that of the triplet.[2] For example, singlet diarylcarbenes are thought to add stereospecifically to olefins and to insert into the O–H bonds of alcohols. By contrast, triplet carbenes are believed to add nonstereospecifically to olefins and to be efficient hydrogen-abstracting agents.[2-14]

The notion that there are sharp distinctions between the chemistry of singlet and triplet diarylcarbenes is widely accepted. However, some of the experimental evidence is equivocal. For example, the optical spectra due to triplet diphenylcarbene,[6,9,18] 1-naphthylcarbene,[19] and fluorenylidene[14] are all quenched by methanol, which is supposedly a singlet quencher. This has led investigators to propose that the singlet and triplet states of these carbenes are linked by efficient equilibria,[4] Scheme I.

Proposals of this kind would certainly gain more credibility if diarylcarbenes could be discovered where the singlet and triplet states could be shown to carry out the simple chemistry that was expected of them.

In an elegant study[20] published in 1964, Zimmerman and Paskovich investigated the chemistry of dimesitylcarbene, I. On the basis of product studies, they concluded that the triplet, once formed, could not readily access the singlet state. We now report, a detailed kinetic study of the reactions of this carbene and find a clean separation between the chemistries of its singlet and triplet states.



I

Experimental Section

Materials. Dimesityldiazomethane was synthesized and purified according to the literature method.[20] Cyclopropane (Aldrich "gold label" grade) and 1,3-cyclohexadiene were commercially available and were used as received. *cis*-2-Pentene was passed through basic alumina and then distilled. Methanol and 1-propanol were purified by distillation from calcium hydride. Benzene was treated with concentrated sulfuric acid. It was washed with aqueous sodium bicarbonate solution and water and finally distilled from calcium hydride.

Table I. Products from the Photolysis of Dimesityldiazomethane (II) in Various Solvents

solvent	[II], M	temp, °C	product	yield,[a] %
cyclopentane	7.2×10^{-3}	−78	III	70
			VI	30
cyclopentane	3.6×10^{-2}	25	III	60
			VI	10
			VII	≤5[b]
benzene[c]	7.2×10^{-3}	140	VII	70
methanol	2.4×10^{-2}	25	IX	90
1-propanol	3.6×10^{-2}	25	X	80
1,3-cyclohexadiene	3.6×10^{-2}	25	XI	90
cis-2-pentene	3.6×10^{-2}	25	III	50
			XII	25
			XIII	25

[a] Yield of isolated material on the basis of starting diazo compound. [b] Estimated from the NMR spectrum of the crude product mixture. [c] Thermolysis in a sealed tube.

Product Studies. A number of product studies were carried out under conditions which were similar to those used in laser flash photolysis experiments (vide infra). Typically, solutions of dimesityldiazomethane (10^{-2}–10^{-3} M) were degassed by using freeze–pump–thaw cycles and sealed in Pyrex ampules. They are irradiated with a visible light source until the characteristic pink color of the diazo compound had disappeared. Approximately 20–30 mg of dimesityldiazomethane was used in each experiment.

After photolysis, the ampules were opened and the solvent and or substrate was removed by bulk-to-bulb distillation under vacuum. The crude product mixtures were chromatographed on silica gel columns or on preparative silica gel thin layer chromatography plates with ether (5% v/v) in hexane as eluent. The isolated products were identified by mass spectrometry and by NMR.

Products II, III, VII, and VIII (vide infra) have been characterized previously.[20] The samples prepared in our laboratory had NMR spectra that were identical with those previously reported, and each showed a parent ion in its mass spectrum. In addition, II and III were further characterized by X-ray crystallography.[21]

Dimesitylmethane, VI, was identified by NMR and GC/MS. VI: (solvent, CCl_4; standard, Me_4Si) *o*-CH_3, s, δ 2.0 (12 H); *p*-CH_3, s, δ 2.2 (6 H); –CH_2–, s, δ 3.8 (2 H); *m*-H, s, δ 6.5 (4 H); GC/MS *m/e* 252. IX: NMR *o*-CH_3, s, $\delta = 2.1$ (12 H); *p*-CH_3, s, δ 2.2 (6 H); CH_3, s, δ 3.2 (3 H); C-H, s, δ 5.5 (1 H); *m*-H, s, δ 6.6 (4 H); GC/MS *m/e* 282. X: NMR –CH_3, t, δ 0.84 (3 H); –CH_2–, m, δ 1.58 (2 H); *o*-CH_3, s, δ 2.1 (12 H); *p*-CH_3, s, δ 2.2 (6 H); *o*-CH_2, t, δ 3.3 (2 H); C–H, s, δ 5.7 (1 H); *m*-H, s, δ 6.7 (4 H); GC/MS 310. Compound **XI** was identified by GC/MS by using chemical ionization *m/e* 331 (p + 1) and by NMR: *o*-CH_3, s, δ 2.2 (12 H); *p*-CH_3, s, δ 2.3 (6 H); *m*-H, s, δ 6.8 (4 H); m, δ 5.7 (2 H); m, δ 1.3–1.8 (6 H). Compounds XII and XIII were analyzed by GC/MS, and each gave *m/e* 320. They were separated from the reaction mixture, but not from each other, by thin layer chromatography, and the NMR spectrum of the combination showed *o*-CH_3, s, δ 2.1 (12 H); *p*-CH_3, s, δ 2.2 (6 H); *m*-H, s, δ 6.8 (4 H); m, δ 1.2–2 (10 H).

Laser Flash Photolysis. The equipment used on these experiments has been described in detail elsewhere[22] with the exception that pulses (308 nm, 10 mJ, and 8 ns width) from a lumonics excimer laser were used to photolyze the samples. Laser flash photolysis experiments were generally carried out on samples that had been purged with nitrogen to remove dissolved oxygen. Solutions were flowed continuously through the sample cell so as to avoid sample depletion and the accumulation of any light-absorbing products.

Results and Discussion

Dimesitylcarbene was originally investigated to probe the effects of steric crowding on the chemistry of a carbene. In their pioneering study,[20] Zimmerman and Paskovich showed that photolysis of dimestiyldiazomethane (2×10^{-3} M) in cyclopropane at −78 °C gave sterically congested olefin III in 98% yield but did not give rise to the less crowded azine IV even though this compound was perfectly stable under the reaction conditions, reactions 2 and 3. This prompted these authors to suggest that the ortho methyl groups forced the carbene to adopt a structure that enhanced the triplet–singlet energy gap.

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$$\underset{\text{II}}{(\text{Mes})_2\text{C}{=}\overset{+}{\text{N}}{=}\overset{-}{\text{N}}} \xrightarrow{h\nu} \underset{\text{I}}{(\text{Mes})_2\text{C}:} + \text{N}_2 \qquad (1)$$

$$(\text{Mes})_2\text{C}: + (\text{Mes})_2\text{C}: \rightarrow \underset{\text{III}}{(\text{Mes})_2\ \text{C}{=}\text{C}(\text{Mes})_2} \qquad (2)$$

$$(\text{Mes})_2\text{C}: + (\text{Mes})_2\text{C}{=}\overset{+}{\text{N}}{=}\overset{-}{\text{N}} \rightarrow \underset{\text{IV}}{(\text{Mes})_2\text{C}{=}\text{N}{-}\text{N}{=}\text{C}(\text{Mes})_2} \qquad (3)$$

$$(\text{Mes}) = 2,4,6\text{-trimethylphenyl}$$

With the assumption that I has a triplet ground state, the chemistry was easily rationalized. Olefin III was formed through a triplet–triplet reaction yet IV could not be formed since it would have involved reaction of the triplet carbene with the singlet diazo compound, which is spin forbidden as a single-step process. Of course these results are in sharp contrast with the chemistry normally observed for diarylcarbenes which, despite their triplet ground states, readily form azines[2] through a mechanism that is presumed to be analagous to that shown in Scheme I.

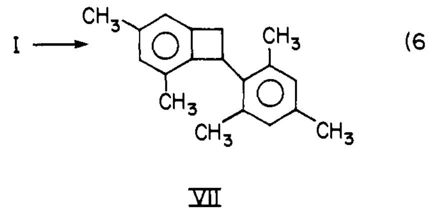
We have repeated these preparative studies using cyclopentane as solvent under conditions that were similar to those used in our laser flash photolysis experiments (vide infra) and have confirmed the earlier observations.[20] The results are shown in Table I and since relatively small quantities of II (ca. 30 mg) were used product yields are quoted to the nearest 5%. Tetramesitylethylene, III, was found to be the major product and is indeed sterically congested. Its X-ray structure[21] showed that the steric crowding caused distortion of the basic olefinic structure and forced the mesityl groups to adopt conformations that minimized the *o*-methyl interactions. Dimesitylmethane, VI, was formed in ca. 30% yield. This product was apparently not detected in the earlier study[20] and presumably arises via reactions 4 and 5.

$$\text{I} + c\text{-C}_5\text{H}_{10} \rightarrow \underset{\text{V}}{(\text{Mes})_2\dot{\text{C}}\text{H}} + c\text{-C}_5\text{H}_9 \qquad (4)$$

$$\text{V} + c\text{-C}_5\text{H}_{10} \rightarrow \underset{\text{VI}}{(\text{Mes})_2\text{CH}_2} + c\text{-C}_5\text{H}_9 \qquad (5)$$

Evidence in support of this mechanism was obtained by photolyzing a solution of I (10^{-4} M) while it was flowed (4 mL/min) through the cavity of an EPR spectrometer. A strong spectrum of a transient radical was obtained which we tentatively assign to V. While there were too many overlapping lines for a unique spectral assignment to be made, it was possible to discern a hyperfine splitting of ca. 15 G due to a single hydrogen which is typical of splittings observed for $a^{\text{H}\alpha}$ in diarylmethyl radicals.[23]

Thermolysis of dimesityldiazomethane in benzene at 140 °C gave cyclobutane VII again in accord with earlier observations, reaction 6.



VII

It should be emphasized that all of the above chemistry is very different from that observed for other diarylcarbenes where, in hydrocarbon solution, azine formation and hydrogen abstraction are the dominant reaction pathways.

In addition to the solution EPR study described above, we have carried out a matrix isolation study of the carbene at −196 °C.[21] The results obtained showed that the *o*-methyl groups forced the carbene to adopt a structure that was far more close to linear than that observed for most other diarylcarbenes. Moreover, X-ray analysis of the structure of II showed that the benzene rings are orthogonal, a conformation which we presume is preserved in the carbene. Both of these structural features will, in principle, tend to enhance the triplet–singlet separation,[24,25] a conclusion which concurs with the inferences drawn from product studies.[20]

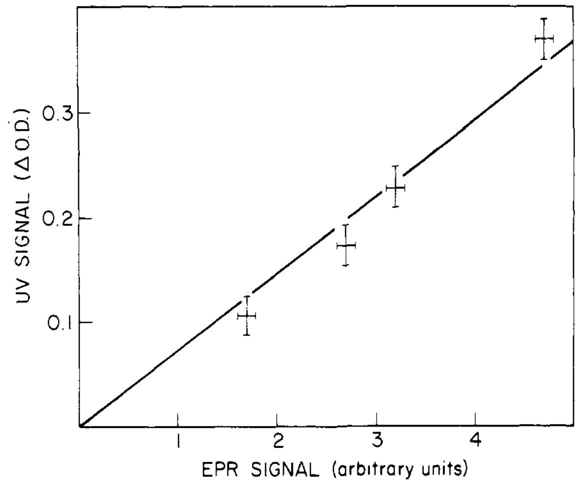


Figure 1. Plot of the amplitudes of UV and EPR signals due to dimesitylcarbene after successive periods of photolysis of dimesityldiazomethane in an isopentane:ether glass.

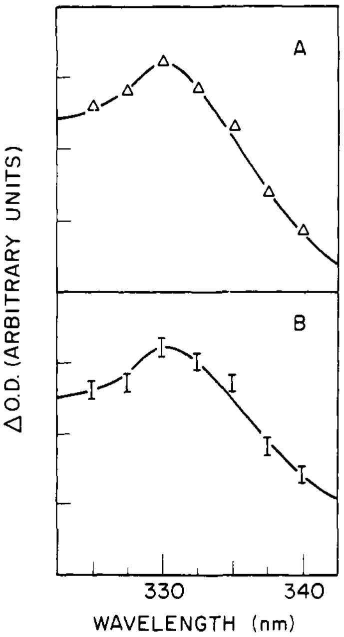


Figure 2. Optical absorption spectrum due to dimesitylcarbene: (A) in benzene at 25 °C; (B) in an isopentane:ether glass at −196 °C.

In order to gain a better understanding of the chemistry of dimesitylcarbene, a number of kinetic studies were carried out with use of laser flash photolysis. However, an essential prerequisite of such studies is that the optical spectra of the intermediates concerned be properly assigned.

We used the approach taken by Trozzolo and Gibbons[26] to assign the optical spectrum of triplet dimesitylcarbene. Photolysis of II (7.3×10^{-3} M) in an isopentane:ether glass (1:1 v/v) at −196 °C gave the EPR spectrum due to triplet dimesitylcarbene.[21] The sample was maintained at −196 °C and was then placed in a UV–vis spectrometer; it showed a new absorption with a maximum

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[23] Berndt, A. In "Landolt-Börnstein"; Fischer, H., Hellwege, K.-H. Eds.; Springer-Verlag: New York, 1977; New Series, Group II, Vol. 9, Part b, Sect. 4.7.1.

[24] In a completely linear diarylcarbene with orthogonal aryl groups, the lowest singlet state may be that which is identical with the triplet with the exception that the two *unpaired* electrons have antiparallel spins. For dimesitylcarbene, which is not strictly linear, there was no EPR or chemical evidence to suggest that a state with such an arrangement of electrons had become low lying *and* was contributing to its chemistry.

[25] Metcalfe, J.; Halevi, E. A. *J. Chem. Soc., Perkin Trans. 2* **1977**, 634. Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

[26] Trozzolo, A. M.; Gibbons, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 239.

at 330 nm. Further photolysis increased the amplitude of the EPR signal and optical absorption in direct proportion (Figure 1). We therefore concluded that the optical absorption at 330 nm was due to triplet dimesitylcarbene. While this experiment is not a definitive proof of the assignment (*post hoc, ergo propter hoc*) it is obviously a much better approach than the norm, where optical absorbance and EPR measurements are carried out on different samples and hence without the test of concentration dependence.

Laser flash photolysis of dimesityldiazomethane (5.1×10^{-5} M) in benzene or cyclopentane gave an absorption spectrum with λ_{max} 330 nm which was essentially identical with that observed in the matrix, Figure 2. We therefore assign this spectrum to triplet dimesitylcarbene. The optical absorption due to the carbene grew within the time response of the instrument (ca. 8 ns). If, as expected, photolysis of II initially yields the carbene in its singlet state, then the rate constant for singlet to triplet intersystem crossing must be $\geq 1.3 \times 10^8$ s^{-1}. This rate constant is consistent with those measured for intersystem crossing in diphenylcarbene (9.1×10^9 s^{-1})[9] and fluorenylidene (3.6×10^9 s^{-1}).[14]

At 25 °C in cyclopentane or benzene solvent, the carbene had a lifetime of ca. 200 μs which is so long in terms of the time scale of the laser instrument that it was impossible to define the kinetic order of the decay. However, since III is the major product under these conditions, decay is presumably bimolecular (reaction 2).

The lifetimes reported above are at least two orders of magnitude greater than those observed for diphenylcarbene (1.7 μs in cyclopentane) and fluorenylidene (1.4 ns in cyclohexane). Clearly, steric crowding in I must be responsible for its longevity.

There was no detectable quenching of the signal due to triplet dimesitylcarbene when *cis*-2-pentene (0.47 M), 1,3-cyclohexadiene (0.52 M), methanol (1.2 M), or 1-propanol (0.67 M) were added to the samples. These types of reagents quench signals due to triplet diphenylcarbene[6,7,9] and fluorenylidene[8,13,14] very efficiently. However, it is important to note that the concentrations of carbene generated in the flash photolysis experiments were relatively high (ca. 10^{-4} to 10^{-5} M) and hence the bimolecular rection of the carbene would have been dominant when inefficient quenchers were present. This reaction was not important under conditions of preparative photolysis (vide infra) where the carbene concentrations were orders of magnitude lower and where carbene–quencher reactions became much more significant. Only oxygen served as an efficient quencher of triplet I. In cyclopentane solution saturated with oxygen (ca. 1.2×10^{-2} M) the lifetime of the carbene was 0.64 μs, indicating that the corresponding ketone was formed with a rate constant of ca. 1.9×10^8 M^{-1} s^{-1} (reaction 7). The fact that only a very small molecule was capable

$$\underset{\text{triplet}}{\text{I}} + O_2 \rightarrow \underset{\text{VIII}}{(Mes)_2CO} \tag{7}$$

of reacting with dimesitylcarbene again supports the notion that it is steric crowding which makes this carbene so persistent.

While triplet dimesitylcarbene was not quenched by standard organic reagents, its precursor, which we assign as the singlet carbene, reacted readily with methanol, 1-propanol, and 1,3-cyclohexadiene. This was evidenced by decreases in the quantum yields for triplet formation when these reagents were present. The Stern–Volmer type of approach was used to analyze the kinetics of these reactions. The ratio of quantum yields for triplet formation in the absence of quencher and in its presence, ϕ^0/ϕ, was plotted against quencher concentration, eq 8, where k_q is the rate constant for the reaction in question and τ_s is the singlet lifetime.

$$\phi^0/\phi - 1 = k_q\tau_s[\text{quencher}] \tag{8}$$

The corresponding plot for methanol is shown in Figure 3. No evidence was found for curvature in the plot for methanol quenching as was previously observed for phenylchlorocarbene where preferential reaction with methanol oligomers took place.[27] However, the scatter of the experimental points which is inherent in this approach may have masked such an effect. With $\tau_s \leq$ 8ns (vide supra) the k_q values were found to be $\geq 1.8 \times 10^7$ M^{-1} s^{-1} (methanol), $\geq 2.2 \times 10^7$ M^{-1} s^{-1} (1-propanol), and $\geq 3.0 \times 10^7$ M^{-1} s^{-1} (1,3-cyclohexadiene).

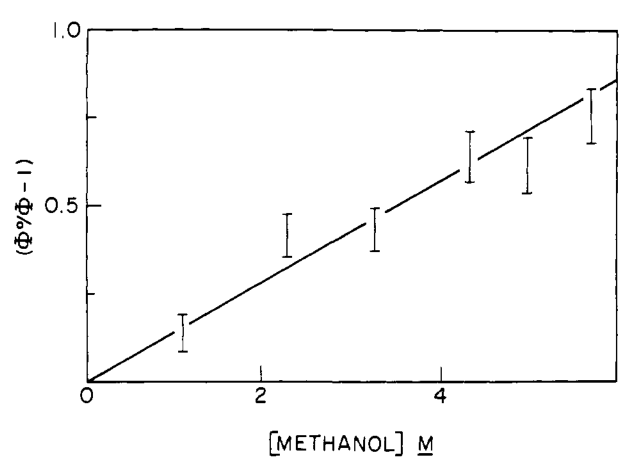
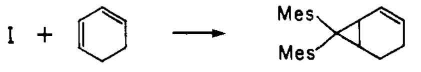


Figure 3. Stern–Volmer plot for the reaction of singlet dimesitylcarbene with methanol.

To confirm expectations about the products formed in these quenching reactions, dimesityldiazomethane (0.038*M*) was photolyzed at 25 °C in methanol, 1-propanol, and 1,3-cyclohexadiene. The Stern–Volmer plots showed that, when these substrates were present as solvents, the quantum yield for triplet formation was effectively nil, i.e., the singlet was scavenged quantitatively. The products are shown in reactions 9–11, and the yields are reported

$$\underset{\text{singlet}}{\text{I}} + CH_3OH \rightarrow \underset{\text{IX}}{(Mes)_2CHOCH_3} \tag{9}$$

$$\underset{\text{singlet}}{\text{I}} + n\text{-PrOH} \rightarrow \underset{\text{X}}{(Mes)_2CHO(n\text{-Pr})} \tag{10}$$



SINGLET (11)

in Table I. They were isolated by thin-layer chromatography and were identified by NMR and mass spectrometry. While the NMR spectrum of XI was fairly complicated, it nevertheless showed absorptions due to only 2 olefinic hydrogens, thus ruling out the possibility that the reaction involved insertion of the carbene into a C–H bond of the cyclohexadiene. 1,3-Cyclohexadiene was itself substantially photodimerized during the photolysis.

Since methanol does not quench triplet dimesitylcarbene, but efficiently quenches the singlet, it follows that triplet–singlet intersystem crossing is not a facile process for this carbene.

$$\underset{\text{triplet}}{\text{I}} \rightarrow \underset{\text{singlet}}{\text{I}} \tag{12}$$

These observations support a similar conclusion drawn from the failure of the carbene to form azine and its proclivity to dimerize (vide supra).

Attempts were made to quench singlet and triplet dimesitylcarbene with use of *cis*-2-pentene as a reagent. Initial experiments suggested that the singlet was scavenged by this reagent. However, product studies showed that this quenching was due entirely to the reaction of the carbene with 1-propanol that was an impurity in the commercially available *cis*-2-pentene. This result emphasizes the importance of product studies of all flash photolysis investigations of carbenes.

Carefully purified *cis*-2-pentene may have barely quenched singlet dimesitylcarbene although the experimental errors in the experiment made this result equivocal. In addition, there was no evidence for significant triplet quenching in the laser flash photolysis experiment where the concentration of the carbene is relatively high and hence where the carbene–carbene reaction tended to dominate. However, irradiation of dimesityldiazomethane, II (0.036 M), in *cis*-2-pentene with a 500W reflector flood lamp (Sylvania R2) gave approximately equal yields of two products with the same *m/e* value of 321 (GC/MS with chemical

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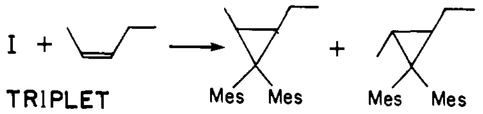
[27] Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

ionization) which we assign to the cis and trans cyclopropanes, reaction 13. These isomers were separated from the reaction mixture but not from each other by thin-layer chromatography. The NMR spectrum of the combination was not sufficiently well resolved in the cyclopropyl region as to allow assignment of the spin–spin interactions. However, there were no signals due to olefinic hydrogen, confirming that the products were indeed cyclopropanes and not olefins formed in a hydrogen abstraction–recombination process.



(13)

In addition to these products, dimer III was formed in ca. 50% yield, reaction 2. The relative yields of cyclopropanes to dimer could be increased by decreasing the intensity of the photolyzing light. These observations imply that when the carbene is present in sufficiently low concentration the cyclopropanation reactions compete with its bimolecular decay.

Summary

The steric influence of the *o*-methyl groups in dimesitylcarbene clearly has a profound effect on its chemistry. The triplet state of the carbene is orders of magnitude less reative toward standard substrates than those of diphenylcarbene or fluorenylidene. Yet, by contrast, the singlet state shows all of the reactivity normally expected for a diarylcarbene.

Singlet-to-triplet intersystem crossing is extremely efficient, while the reverse process is not. The latter is evidenced by the failure of triplet dimesitylcarbene to react with alcohols or the parent diazo compound. The sharp distinctions between the chemistries of the singlet and triplet states imply that there is a substantial free energy separation between them, a situation which is not observed for the other diarylcarbenes that have, so far, been investigated.[6,8–14]

Our earlier EPR observations[21] imply that the *o*-methyl groups of dimesitylcarbene constrain the phenyl rings to be perpendicular and point to a structure for the carbene which is close to linear. This structure is quite different from that of diphenylcarbene which has a bent minimum-energy geometry. However, theory indicates that opening a diarylcarbene to a linear structure requires very little energy.[24,25] It therefore seems reasonable to suppose that the steric interaction which confers a more linear structure on dimesitylcarbene does not lead to substantial destabilization of the triplet ground state relative to that of diphenylcarbene. In fact, the most significant change that occurs on opening the central C–C–C angle in a diarylcarbene is that the singlet state becomes substantially destabilized leading to an enhanced triplet singlet gap,[24,25] which is entirely consistent with the chemistry observed for dimesitylcarbene.

Since the triplet state of dimesitylcarbene is probably slightly destabilized with respect to that of diphenylcarbene, it follows that its relatively low reactivity must reflect steric protection of the carbene center by the *o*-methyl groups. If we take triplet diphenylcarbene to be a standard for diarylcarbene reactivity, then dimesitylcarbene can be correctly described as being persistent, confirming expectations for the role of steric effects in carbene chemistry established almost 20 years ago.[20]

The present results show that the triplet state of a diarylcarbene is capable of a unique chemistry that does not involve access to the singlet manifold. However, the question still remains as to whether there is a true thermodynamic equilibrium between the singlet and triplet states of other carbenes in which the energy gap between the states is thought to be much smaller.[6,8–14]

Theoretical results[24,25] as well as those herein suggest that the separation of triplet and singlet states in a given diarylcarbene is likely to be very sensitive to the extent to which the carbene center is bent and to the orientation of the aryl groups. Thus, if the triplet–singlet gap is small enough the states may be mixed by molecular vibrations and/or rotations and could easily be perturbed by the approach of solvent or substrate molecules.

In conclusion, the present work shows that it is possible to discover diarylcarbenes for which the chemistries of the singlet and triplet states are quite distinct. However, this should not be taken to imply that these distinctions necessarily apply to all diarylcarbenes.

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