Dimesitylcarbene: The Distinct Chemistries of its Singlet and Triplet States

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Dimesitylcarbene is unique amongst the diarylcarbenes thus far investigated since its triplet state cannot readily convert into the singlet state.

The singlet states of diarylcarbenes are thought to insert into the O-H bonds of alcohols and to add stereospecifically to olefins. By contrast, their triplet ground states are thought to be efficient hydrogen abstracting agents and are believed to add non-stereospecifically to olefins.¹⁻¹²

The experimental data supporting these hypotheses are equivocal. For example, optical absorption spectra due to the triplet states of diphenylcarbene,^{6,8,13} fluorenylidene,^{11,12} and 1-naphthylcarbene¹⁴ are all quenched by methanol. To explain these results, investigators have suggested that the triplet and singlet states are in thermal equilibrium, reactions (1) and (2). This description of the mechanism rests on the assumption that it is the spin-state of the carbene which controls its mode of reaction. However, the experimental observations can simply be interpreted in terms of a direct reaction between the triplet state and alcohol.⁴ Clearly, this paradox would be resolved to some extent if diarylcarbenes could be discovered

$$\begin{array}{c} Ar_2C: \rightleftharpoons Ar_2C: \qquad (1)\\ singlet \qquad triplet \\ MeOH \\ \downarrow \\ Ar_3CHOMe \qquad (2) \end{array}$$

where the triplet state carried out a chemistry which was completely distinct from that of the singlet, and hence, which reacted without conversion into the singlet state. In this work we have developed the observation¹⁵ that dimesitylcarbene, in sharp contrast to other diarylcarbenes, did not react with its parent diazo compound to give azine, reaction (3), but dimerized to give olefin, reaction (4). This result was explained¹⁵ by proposing that the triplet ground-state¹⁶ could not convert into the singlet state so that reaction with the singlet diazo compound could not take place, *cf.* reactions

$$(Mes)_{2}C: + (Mes)_{2}CN_{2} \rightarrow (Mes)_{2}C-N=N-C(Mes)_{2} \qquad (3)$$
$$2(Mes)_{2}C: \rightarrow (Mes)_{2}C=C(Mes)_{2} \qquad (4)$$
$$Mes = mesitvl$$

(1) and (2). The carbene simply decayed by the triplet-triplet process, reaction (4).

Photolysis of dimesityldiazomethane $(7 \times 10^{-3} \text{ M})$ in an isopentane-ether glass at $-196 \,^{\circ}\text{C}$ gave an e.s.r. spectrum due to triplet dimesitylcarbene¹⁶ and a new optical absorption at 330 nm. Observations made on a single sample showed that the intensities of the e.s.r. and optical signals grew in direct proportion with successive increments of photolysis. Laser flash photolysis of dimesityldiazomethane ($5 \times 10^{-5} \text{ M}$) in benzene or cyclopentane at 25 °C gave the same optical absorption spectrum and we assign this to triplet dimesityl-carbene, reaction (5). The carbene had a lifetime of *ca.* 200 μ s

$$(Mes)_{2}CN_{2} \xrightarrow{h\nu} (Mes)_{2}C: + N_{2}$$
(5)
triplet

in both solvents and decayed to give a dimer¹⁵ which we were able to isolate in 70% yield, reaction (4). The signal due to the carbene was quenched by oxygen $(1.2 \times 10^{-2} \text{ M})$ to give dimesityl ketone¹⁵ (g.c.-mass spectrometry) which is again a triplet-triplet reaction [reaction (6)].

$$(Mes)_2C: + O_2 \rightarrow (Mes)_2C=O$$
 (6)
triplet

The triplet lifetime of dimesitylcarbene, in contrast to other diarylcarbenes, was essentially unaffected by addition of methanol (1.2 M). However, methanol reduced the quantum yield for triplet formation by scavenging the singlet carbene, reactions (7) and (8). The rate constant for singlet quenching



 k_8 was measured with respect to that for intersystem crossing, k_7 in a Stern-Volmer experiment, equation (9), where Φ and Φ^0 are respectively the quantum yields for triplet formation

$$(\Phi^0/\Phi) - 1 = (k_8/k_7)$$
 [MeOH] (9)

in the presence and absence of methanol. The experiment gave $k_8/k_7 = 0.14^{.17}$ Since the triplet is completely formed within the laser pulse (8 ns), it follows that $k_7 > 1.3 \times 10^8$ and hence $k_8 > 1.8 \times 10^7 \,\mathrm{l\,mol^{-1}\,s^{-1}}$. In a preparative experiment with methanol as solvent, the expected ether was isolated in 90% yield, reaction (8). Similar experiments with propan-1-ol gave $k_8 > 2.2 \times 10^7 \,\mathrm{l\,mol^{-1}\,s^{-1}}$ and an 80% yield of isolated ether.

Laser flash photolysis experiments showed that *cis*pent-2-ene was an inefficient quencher of both singlet and triplet dimesitylcarbene. However, photolysis at low light intensities of dimesityldiazomethane (0.036 M) in *cis*-pent-2ene gave tetramesitylethylene, reaction (4) (yield *ca.* 50%, g.c.-mass spectrometry), and cyclopropanes (I) and (II) (yield *ca.* 25% of each), reaction (10). The yield of olefin was increased at the expense of the cyclopropanes in an experiment carried out at higher light intensities and hence at

$$(Mes)_2 C: + (Mes)_2 C + (Mes)_2 C$$

$$I \qquad II \qquad II$$
(10)

higher carbene concentration. This indicates that all of the products were derived from the triplet carbene.

The experiments described above demonstrate that singlet and triplet dimesitylcarbene carry out quite distinct reactions and that the triplet carbene does not convert into the singlet state. E.s.r. studies¹⁶ support these observations and show that the carbene has a structure which is almost optimal for the stabilization of the triplet state. The clear distinctions between the chemistries of singlet and triplet dimesitylcarbene do not prove that this will be the case for other diarylcarbenes. Recent results¹³ suggest that when the singlettriplet gap is small, mixing of the states can be induced by the approach of a substrate molecule which may be assisted by rotation of the aryl groups.¹⁸ Clearly the subject warrants more detailed investigation.

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