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# LASER FLASH PHOTOLYSIS STUDY OF 10,10-DIMETHYL-9-ANTHRYLIDENE, A CARBENE WITH NEARLY DEGENERATE SINGLET AND TRIPLET STATES

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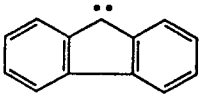
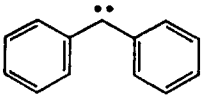
**10,10-Dimethyl-9-anthrylidene (DMA) was studied by laser flash photolysis (LFP) techniques. LFP of the requisite diazo precursor in pentane or carbon tetrachloride produced transient spectra attributed to the hydrocarbon and monochlorinated diarylmethyl radicals, respectively. In the presence of pyridine and oxygen, ylides were formed upon LFP of 10,10-dimethyl-9-diazoanthrone. However, ylides are not formed in acetonitrile or acetone. The carbene itself was not detected by transient absorption spectroscopy. The absolute rate constants for reaction of DMA with pyridine, methanol and triethylsilane are $1{\cdot}96 \times 10^9$, $1{\cdot}8 \times 10^{10}$, and $1{\cdot}0 \times 10^8$ l mol$^{-1}$ s$^{-1}$, respectively. It is concluded that the singlet and triplet states of DMA are essentially degenerate.**

## INTRODUCTION

The dynamics of diarylcarbenes have been extensively studied in the past decade by laser flash photolysis (LFP) techniques,[1] which have revealed interesting structure–reactivity relationships. For example, two closely related carbenes, diphenylcarbene (DPC) and fluorenylidene (Fl), behave very differently in alkanes. The lifetime of Fl in cyclohexane is only 1 ns,[2] whereas that of DPC is several microseconds in this solvent.[3] Although Fl is known by EPR spectroscopy to have a ground triplet state,[4] the chemistry of Fl in cyclohexane proceeds almost entirely through the low-lying singlet state.[5] On the other hand, the chemistry of DPC in this solvent can be explained as being due to reactions of the ground-triplet state alone.[5] These results have been interpreted to mean that the singlet triplet energy separation, $\Delta H_{ST}$, is much smaller in Fl than in DPC.[1,2,5] To establish whether the smaller value of $\Delta H_{ST}$ is due to the smaller bond angle of Fl or related to the differences in their $\pi$ electronic systems (alternant versus non-alternant), we have studied 10,10-dimethyl-9-anthrylidene (DMA), a carbene with an alternant $\pi$ system as in DPC, but constrained within a small bond angle. The LFP data demonstrate that the singlet and triplet states of DMA are essentially degenerate and indicate that the smallest $\Delta H_{ST}$ of fluorenylidene is a result of its small bond angle.



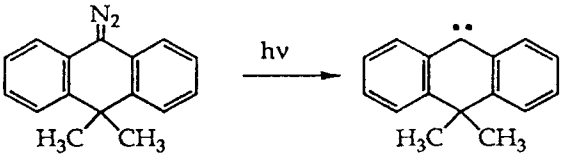
Fl



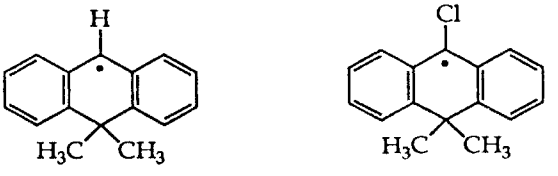
DPC

## RESULTS AND DISCUSSIONS

LFP of 10,10-dimethyl-9-diazoanthracene (DMDA)[6] in *n*-pentane produces the transient absorption spectrum in Figure 1, attributed to radical **1**.[7] LFP of DMDA in




DMDA DMA




**1** **2**

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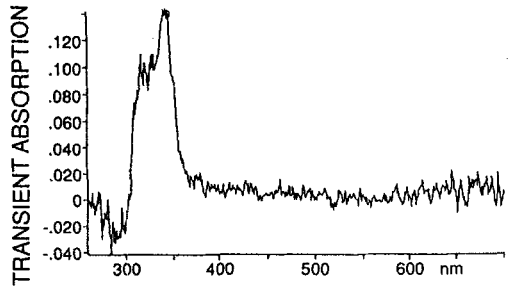



Figure 1. Transient spectrum of radical **1** produced by LFP of DMDA in pentane

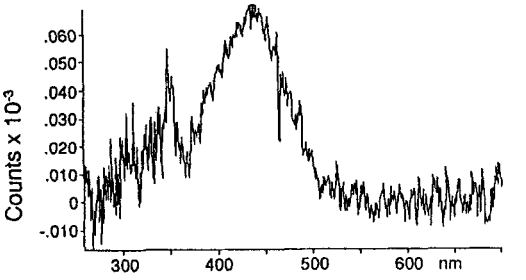



Figure 3. Transient spectrum of carbonyl oxide **3** produced by LFP of DMDA in pentane containing oxygen

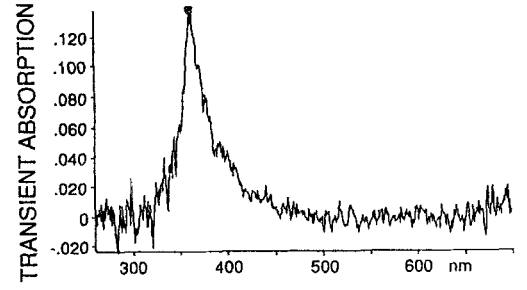



Figure 2. Transient spectrum of radical **2** produced by LFP of DMDA in carbon tetrachloride

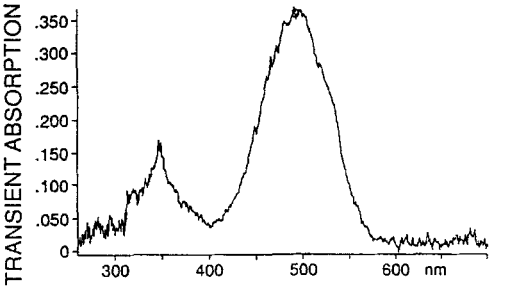
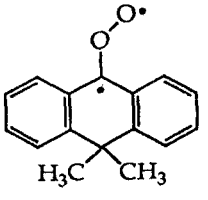


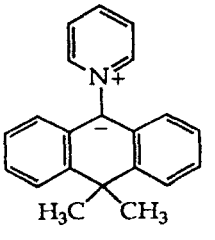

Figure 4. Transient spectrum of ylide **4** produced by LFP of DMDA in pentane containing pyridine

carbon tetrachloride produces the transient spectrum of radical **2** (Figure 2).

Transient absorption spectra attributable to $^3$DMA were not observed in either solvent. It was possible to intercept $^3$DMA with oxygen, in pentane, to form the carbonyl oxide **3**,[8] and to trap $^1$DMA with pyridine to form the ylide **4**[9] (Figures 3 and 4, respectively). In contrast to fluorenylidene, ylides were not observed on LFP of DMDA in acetone or acetonitrile.[1,2]




**3**




**4**

The rate of formation of **4** was exponential and was fitted to yield an observed pseudo-first-order rate constant $k_{obs}$. It has been demonstrated that singlet and triplet states of several arylcarbenes (DPC,[10] phenylcarbene[11] and Fl[12] in some solvents) are rapidly equilibrating and can be treated as a single kinetic unit. This allows us to equate $k_{obs}$ with the elementary rate constants of Scheme 1 as given in the equation[13]

$$k_{obs} = k^1_{PYR}K[PYR] + k_0 \quad (1)$$

where $k^1_{PYR}$, and K are defined in Scheme 1 and $k_0$ is the total of all processes which consume DMA in pentane in the absence of pyridine. A plot of $k_{obs}$ versus pyridine is linear (Figure 5), revealing that

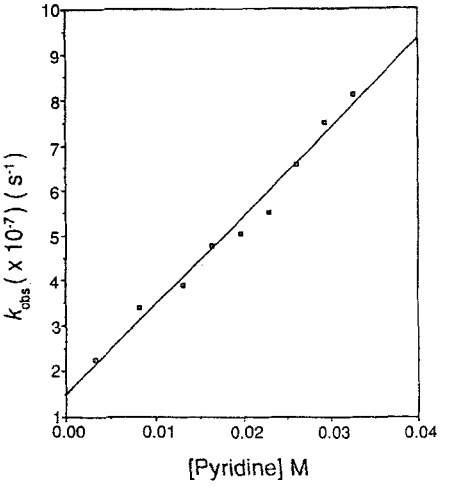
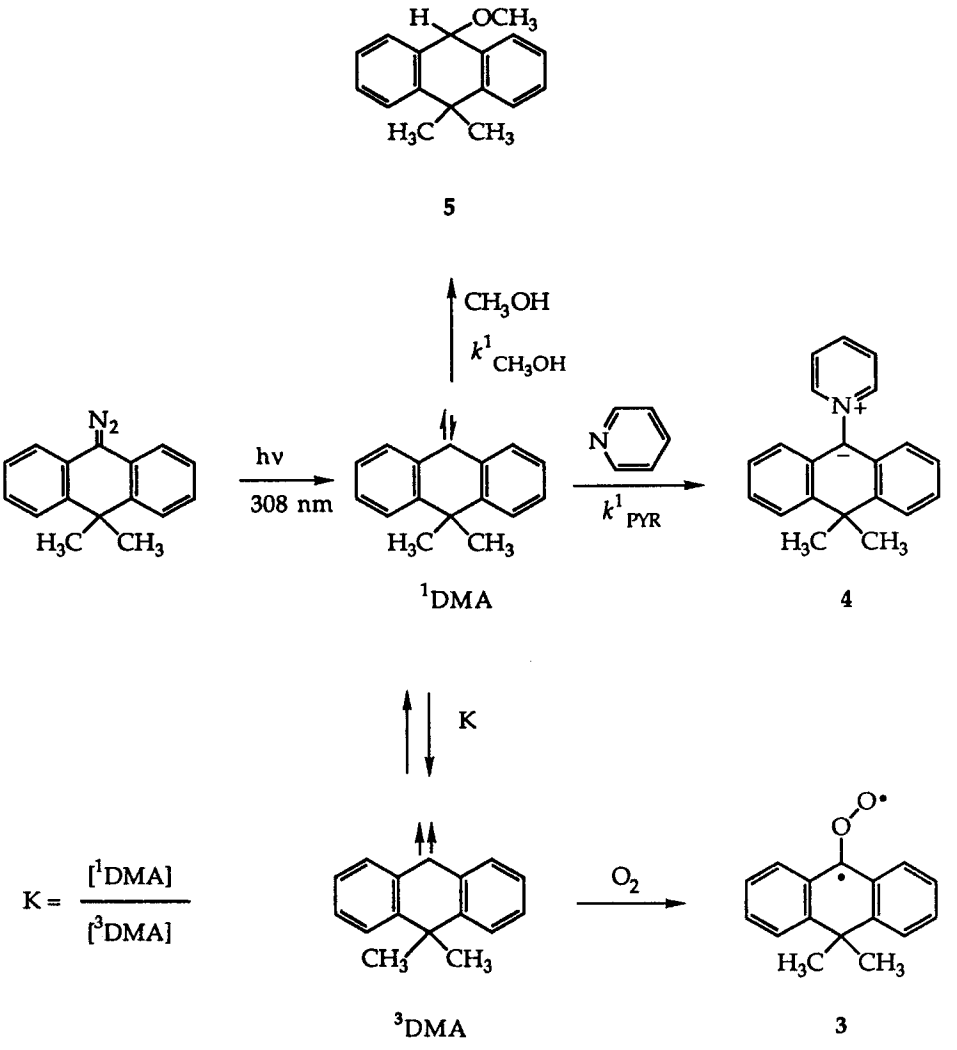



Figure 5. Plot of $k_{obs}$ versus [PYR] (see text)




Scheme 1

$k^1_{PYR}K = 1{\cdot}96 \times 10^9$ l mol$^{-1}$ s$^{-1}$ and that the lifetime of DMA in pentane is 62 ns when [PYR] = 0. As singlet to triplet intersystem crossing (ISC) in DPC and Fl is complete within 1 ns,[2,14] it seems certain that $^1$DMA and $^3$DMA are in a rapid equilibrium in pentane at ambient temperature.

It was possible to monitor the effect of a singlet quencher, methanol, on $k_{obs}$. A plot of $k_{obs}$ versus [methanol] at constant [pyridine] is given in Figure 6, which reveals that $k^1_{CH_3OH}K = 1{\cdot}8 \times 10^{10}$ l mol$^{-1}$ s$^{-1}$. A similar experiment with triethylsilane yields $k_{Et_3SiH} = 1{\cdot}0 \times 10^8$ l mol$^{-1}$ s$^{-1}$.

This analysis assumes that only $^1$DMA reacts with pyridine and methanol. This type of pre-equilibrium mechanism was first postulated by Bethel *et al.*[15] However, nearly all of the mechanistic data available for diarylcarbenes are consistent with the presence of a single reactive intermediate, a species which can react to form products traditionally ascribed to the reactions of both singlet and triplet carbenes. In this view, $^3$DMA reacts directly with pyridine or methanol to form products as a result of a crossing of singlet and triplet surfaces along the reaction coordinate. This mechanism was first proposed by Griller, Nazran and Scaiano[16] for the reaction of $^3$DPC with methanol. They demonstrated that the kinetics observed for the $^3$DPC–methanol reaction are inconsistent with Bethell *et al.*'s mechanism. The present work indicates that the

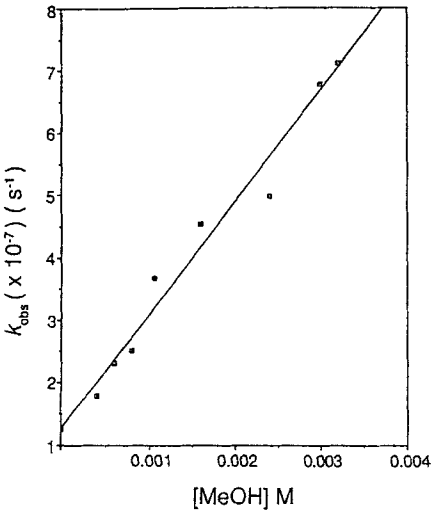
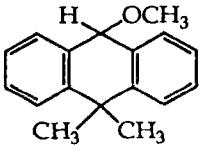



Figure 6. Plot of $k_{obs}$ versus [$CH_3OH$] at constant [PYR] (see text)

singlet and triplet surfaces of DMA are very close in energy. The surfaces are so close in energy that $\Delta H_{ST} \approx 0$. Hence in the DMA system there is no meaningful difference between Bethell *et al.*'s pre-equilibrium mechanism and Griller *et al.*'s surface crossing mechanism.

### Gas chromatographic–mass spectrometric (GC–MS) analysis

Several solutions of DMDA were photolyzed for extended periods and the mixtures analyzed by GC–MS. On photolysis of DMDA in neat methanol, compound **5**, the expected product of OH insertion, is formed fairly cleanly (86%) along with only small amounts of **6** (9%) and **7** (5%).

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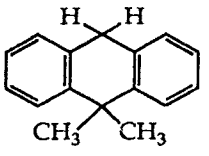


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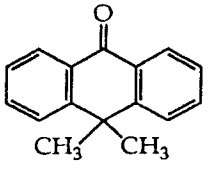
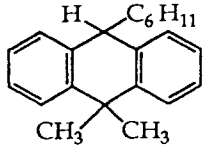



7

From the available kinetic data, we can calculate that the lifetime of $^3$DMA in pentane containing 0·025 M methanol is 2·2 ns. This lifetime should be sufficiently long to allow complete equilibration of singlet and triplet DMA. The product distribution obtained in dilute methanol is virtually identical with that obtained in neat methanol (78% yield of **5**) and demonstrates that spin-equilibrated DMA reacts with alcohol predominantly by OH insertion.

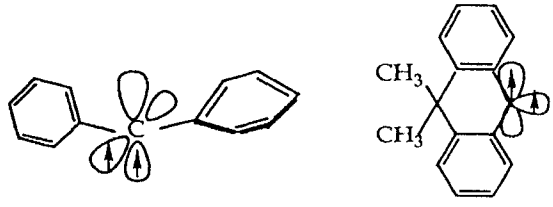
Photolysis of DMDA in cyclohexane gives **8**, the product of formal CH insertion as the major product (59%), along with significant amounts of **6** (20%) and **7** (19%).




8

When DMDA is decomposed in 1:1 (v/v) $C_6H_{12}$–$C_6D_{12}$, the **8**-$d_0$/**8**-$d_{12}$ ratio is 4·6. This isotope effect is too large for a singlet carbene CH insertion reaction[5,11a,17] and is comparable to isotope effects observed in triplet carbene hydrogen atom abstraction reactions.[18] Hence the data demonstrate that the lifetime of $^3$DMA in alkanes is controlled by triplet carbene reactions. $^3$DMA is much more potent in the abstraction of hydrogen from a CH bond of an alkene than is triplet diphenylcarbene (DPC).[3]

The geometry of $^3$DPC in single crystals has been deduced by ENDOR,[19] but the geometry of the carbene in solution or in the gas phase is unknown. It is likely for steric reasons, however, that DPC has a wide bond angle at the carbene carbon and to be non-planar:




Thus AM1 calculations indicate that each unpaired electron of $^3$DPC is likely to be in a hybrid orbital with a considerable amount of p character and some resonance interaction with an aryl ring.[20] In $^3$DMA, however, it is possible that one orbital is $sp^2$ and the other is pure p. An in-plane orbital of $^3$DMA is $\sigma$ in nature and may have a reactivity comparable to that of phenyl radical.[21]

Li and Schuster[22a] have had great success in correlating experimental values of $\Delta H_{ST}$ of aryl substituted

carbenes with the predictions of the MINDO/3 algorithm. MINDO/3 predicts that the $\Delta H_{ST}$ values of DMA, Fl and DPC are 15·1, 16·7 and 36·8 kJ mol$^{-1}$, respectively. Although we find that MINDO/3 orders the $\Delta H_{ST}$ value of these carbenes correctly, the singlet–triplet enthalpy gap of DMA is, as noted previously,[22] smaller than predicted.

## CONCLUSIONS

The fact that $^3$DMA can be detected at 10 K by EPR spectroscopy[6] demonstrated that $^3$DMA is either the ground state of the carbene or within a few kJ mol$^{-1}$ of the ground state and that $K \leqslant 1$. The low-temperature emission spectrum is also consistent with a triplet ground state of this carbene.[7] However, product studies reveal that it is $^1$DMA that is captured by methanol. As $k^1_{CH_3OH}$ must be less than or equal to a diffusion-controlled rate constant ($2 \times 10^{10}$ l mol$^{-1}$ s$^{-1}$), Figure 6 demonstrates that the equilibrium population of $^1$DMA must be fairly large and that $K \approx 1$ at ambient temperature. The singlet and triplet states of DMA are essentially degenerate. The singlet–triplet splitting of DMA is found to be even smaller than that of fluorenylidene. Apparently the necessarily small and constrained bond angles of Fl and DMA, and perhaps the enforced coplanarity of the two aryl rings, are decisive in lowering the energy of $^1$DMA and $^1$Fl relative to their triplet states, relative to DPC. The results are consistent with the semi-empirical calculation of Li and Schuster.[22a]

## EXPERIMENTAL

The preparation of DMDA[6] and the GC–MS protocols and the LFP system in use at Ohio State University[23] have been described previously.

### ACKNOWLEDGMENT

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