3,6-Dimethoxyfluorenylidene: A Ground-State Singlet Carbene

Carl Chuang, Stephen C. Lapin, Alan K. Schrock, and Gary B. Schuster*

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. Received October 15, 1984

Abstract: Irradiation of 3,6-dimethoxy-9-diazofluorene gives 3,6-dimethoxy-9-fluorenylidene. This carbene was detected in frozen media by low-temperature optical spectroscopy and at room temperature in fluid solution by nanosecond laser techniques. The EPR spectrum of the diazo compound irradiated at low temperature does not show any characteristic triplet carbene signals. The carbene reacts with methyl alcohol at approximately the diffusion-limited rate to give the expected ether. It inserts directly into the carbon–hydrogen bonds of cyclohexane, and it adds to olefins with total retention of stereochemistry. These findings are interpreted to show that the ground state of this carbene is a singlet. The properties of this carbene are compared with those of fluorenylidene, and a correlation of structure and reactivity is suggested.

The chemical and physical properties of fluorenylidene[1] (FL) and several related aromatic carbenes[2,3] have recently been the object of considerable attention. In part, this interest is driven by the desire to probe the structural features that control the chemical properties of these highly reactive, short-lived intermediates. We recently reported results that were interpreted to show that the ground-state triplet of fluorenylidene (^{3}FL) is no more than 1.9 kcal/mol lower in energy than singlet fluorenylidene (^{1}FL), the first electronically excited state of this carbene. This small energy difference permits the rapid reformation of ^{1}FL from ^{3}FL, and, as a consequence, the chemical properties of fluorenylidene show characteristics of both an electrophilic singlet and a radical-like triplet state.[1]

The small energy differences between ^{1}FL and ^{3}FL led us to suspect that the ordering of states might be reversed by substituents that are able to stabilize the singlet more than they do the triplet state.[4] Herein, we report the results of our investigation of the chemical and physical properties of 3,6-dimethoxyfluorenylidene (DMFL) formed from photolysis of 3,6-dimethoxy-9-diazofluorene (DMDAF), eq 1. To the best of our knowledge, DMFL is the
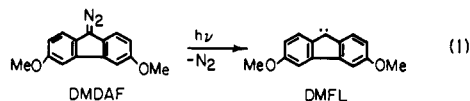

first verified example of a singlet ground-state carbene that does not have a heteroatom bound directly to the carbene carbon atom.[5]

Results

(1) Preparation of DMDAF. DMDAF is a stable, red solid that is conveniently prepared in good yield by mercuric oxide oxidation of the corresponding hydrazone. The synthesis of DMDAF is outlined in eq 2 and the details of the preparation

are presented in the Experimental Section.
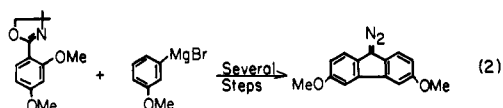
(2) Photolysis of DMDAF in Frozen Media. Irradiation of a dilute solution of DMDAF in a 2-methyltetrahydrofuran (MTHF) glass at 77 K leads to consumption of the diazo compound and the formation of a new species with absorption maxima at 428 and 409 nm, Figure 1A. The new species is stable indefinitely in the glass, but it is irreversibly consumed when the solution is warmed to room temperature. This behavior of the intermediate is consistent with it being the carbene DMFL, the cation formed by protonation of this carbene,[7] or the radical (DMFLH·) formed by hydrogen atom abstraction by the carbene.

Triplet carbenes have characteristic EPR spectra. Irradiation of diazofluorene (DAF)[8] or benzodiazofluorene (BDAF)[3] in frozen media gives easily observed triplet carbene signals. However, irradiation of DMDAF under a range of solvent, concentration, and light intensity conditions does not give the EPR spectrum of the carbene. In particular, irradiation under the conditions that generate the optically detected transient does not produce a detectable triplet carbene EPR signal. Instead, only a small amount of a doublet species (presumably DMFLH·) is observed. It is not possible to reach a firm conclusion from the absence of an EPR spectrum. But, it is clear that the optically detected transient is not the triplet carbene.

It is not likely that the species detected optically at 408 and 429 nm at low temperature is DMFLH·. The 9-fluorenyl radical (FLH·) absorbs strongly at 495 nm,[1] and the methoxy substituents on DMFLH· are not expected to shift this absorption to higher energy. We carried out a series of laser spectroscopic, kinetic, and product studies that similarly indicate that the optically detected species is neither DMFLH· or the cation but that it is most comfortably assigned to the singlet state of the carbene (^{1}DMFL).

(3) Transient Absorption Spectroscopic Analysis of DMDAF. Irradiation of a ca. 5 × 10^{-4} M solution of DMDAF in oxygen-free, anhydrous benzene at room temperature with a nitrogen laser (337 nm, 15 ns, 7 mJ)[9] generates a transient species whose absorption spectrum is shown on Figure 1B. This product is formed within the 15-ns pulse width of the laser, and, under these con-

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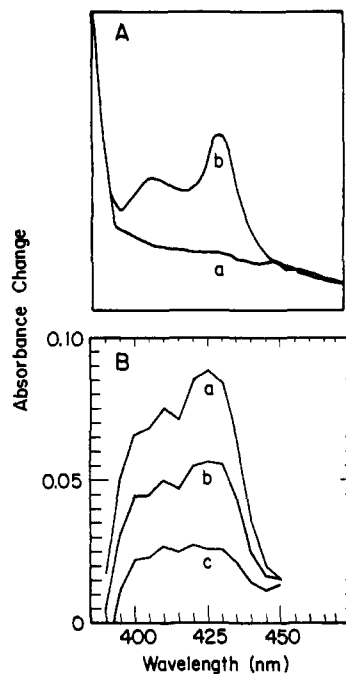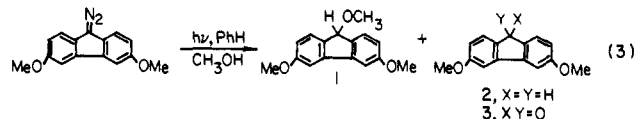(9) Horn, K. A.; Schuster, G. B. *Tetrahedron* **1982**, *38*, 1095.

Properties of 3,6-Dimethoxyfluorenylidene

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Figure 1. (A) Absorption spectrum recorded after irradiation of DMDAF in 2-methyltetrahydrofuran at 77 K (a) and (b) the same sample after warming to room temperature and then refreezing at 77 K. (B) Transient absorption spectra recorded 20 ns (a), 40 ns (b), and 100 ns (c) after irradiation of DMDAF in benzene at room temperature. The spectra were recorded at 5-nm intervals and are reproducible to 0.01 o.d. units.

Figure 2. Pseudo-first-order rate constants (k_{obsd}) for decay of DMFL at 425 nm measured at increasing methyl alcohol concentrations.

Table I. Rate Constants for Reaction of DMFL with Trapping Reagents in Benzene Solution at Room Temperature

reagent	rate constant, $M^{-1} s^{-1}$
CH_3OH	$5.6 \pm 0.3 \times 10^9$
CH_3OD	$4.8 \pm 0.4 \times 10^9$
$(CH_3)_3COH$	$4.1 \pm 0.5 \times 10^9$
$(CH_3)_3CNH_2$	$<1 \times 10^{7\,a}$
$(C_2H_5)_3N$	$<1 \times 10^{7\,a}$
Ph⧹⧸	$4.3 \pm 0.4 \times 10^7$
Ar⧹⧸ (m-F)	$9.8 \pm 0.8 \times 10^7$
Ar⧹⧸ (p-OMe)	$1.6 \pm 0.2 \times 10^7$
Ph⧹⧸CH_3	$1.3 \pm 0.1 \times 10^8$
$(CH_3)_2C=CHCH_3$	$5.2 \pm 0.6 \times 10^7$

^{a} The small value of these rate constants, coupled with difficulties keeping these amines absolutely anhydrous, makes these measurements suspect. The actual bimolecular rate constants are no larger than the reported values.

ditions, it decays by a pseudo-first-order kinetic path with a half-life of 51 ns. Nearly identical results are obtained when irradiation of DMDAF is carried out in acetonitrile ($t_{1/2}$ = 18 ns) solution. Irradiation of the diazo compound in cyclohexane similarly gives the transient product absorbing at ca. 400 and 418 nm. In this solvent, the absorptions decay with a half-life of approximately 11 ns, and a new, very weak, broad absorption with an apparent maximum at ca. 490 nm grows in on this time scale. The second species is likely to be due to, at least in part, DMFLH·. Product studies, see below, also suggest formation of this radical in very low yield.

The spectrum of the transient created by pulsed laser photolysis of DMDAF is similar to that formed by irradiation of the diazo compound in frozen media (compare Figure 1). Thus, we feel that both of these spectra are due to the same reactive intermediate. The chemical properties of this intermediate (see below) are characteristic of those typically assigned to singlet carbenes and not at all what is expected of the radical or cation.

(4) Chemical and Kinetic Properties of DMFL. One of the most characteristic reactions of a singlet carbene is its combination with an alcohol to form an ether.[10] Irradiation of DMDAF (4×10^{-3} M) in benzene containing methyl alcohol (1 M) at 350 nm in a Rayonet Photoreactor gives the expected ether (1) in 65% yield, eq 3. Also formed in this reaction are 3,6-dimethoxyfluorene

(2) and 3,6-dimethoxyfluorenone (3). These latter two products probably arise from photodecomposition of the ether, which ab-
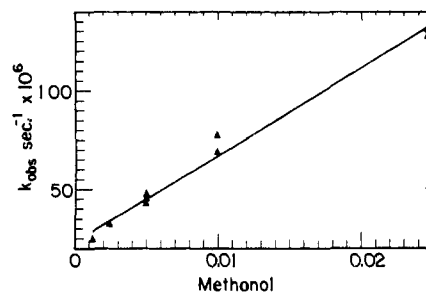
sorbs at appropriate wavelengths, and was observed independently to give these compounds when it is irradiated.[11]

The short-lived transient product formed from photolysis of DMDAF appears to react with methyl alcohol. Irradiation of the diazo compound in benzene containing the alcohol generates the transient species that absorbs at 428 nm. The lifetime of this species decreases as the concentration of alcohol in solution is increased, Figure 2. Least-squares analysis of these kinetic data reveals that the bimolecular rate constant for this reaction ($K_{MeOH}^{C_6H_6}$) is 5.6×10^9 M^{-1} s^{-1}. This rate constant is quite close to that expected for a diffusion-controlled process in benzene.

The kinetic isotope effect on the rate of this reaction when methyl-d_1 alcohol is used is only ca. 1.2. This is in contrast to FL which exhibits an isotope effect of ca. 2.4.[12] This result also supports the notion that this reaction of DMFL proceeds with a rate at or near the diffusion limit. These and other rate constants are summarized in Table I.

The reaction of the transient product with amines is quite helpful in the assignment of its structure. It has been observed[13] that aryl-substituted cations react with amines much faster than they do with alcohols. In contrast, FL reacts with amines more slowly than it does with alcohols.[12] We examined the reaction of the transient product formed from photolysis of DMDAF with *tert*-butylamine and triethylamine. If the transient is the dimethoxyfluorenyl cation, we expect that it would react at least as fast with the amine as with the alcohol. If the transient is the carbene, we expect that the opposite will be true. In fact, the transient product reacts ca. 100 times more slowly with *tert*-butylamine than it does with *tert*-butyl alcohol. For this reason, and

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for several others described below, we feel that the detected transient is the carbene and not the cation.

Irradiation of DMDAF in cyclohexane generates the insertion product **4** and, in contrast to FL,[1b] only minor amounts of apparent radical coupling and disproportionation products **2** and **5** and a trace of the dimeric bis(dimethoxyfluorenylidene) (**6**), eq 4. The
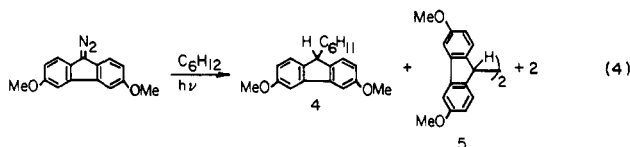

yield of dimeric olefin **6** does not increase when DMDAF in cyclohexane is irradiated with the laser. But this compound is a major product when the diazo compound is photolyzed in benzene. Irradiation of the DMDAF in C_6D_{12} indicates an isotope effect of 1.7 for the decay of the absorptions associated with the carbene. A similar isotope effect is measured for the growth of the absorptions believed to be due to DMFLH·.

Insertion product **4** could in principle arise from coupling of free DMFLH· with a cyclohexyl radical, or it could be a result of direct insertion into a C–H bond of cyclohexane. The former process is characteristic of triplet carbenes; the latter is believed to be a singlet carbene reaction.[10] To distinguish between these two paths for formation of **4**, we irradiated DMDAF in a 1:1 mixture of C_6H_{12} and C_6D_{12}. Analysis of the cyclohexyl insertion product **4** by GC–mass spectroscopy shows that, within experimental error, none of this product can arise from coupling of free radicals. Thus, it appears that the major reaction path for DMFL in cyclohexane is direct insertion—the singlet carbene process. This finding supports the assignment of the detected transient to ^{1}DMFL.

One of the most characteristic and useful reactions of a carbene is the generation of a cyclopropane from addition to an olefin.[10] We examined several examples of the reaction of DMFL with olefins as an aid in the characterization of the reactivity of this carbene.

Irradiation of DMDAF in benzene containing 2 M styrene gives the expected cyclopropane **6** as the exclusive product, eq 5. The rate of reaction of the carbene with styrene is readily determined by monitoring the effect of styrene concentration on the rate of decay of the transient species. As expected, increasing the amount
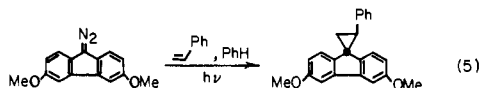
of styrene in solution shortens the lifetime of the transient. Similar experiments were carried out with *p*-methoxystyrene, *m*-fluorostyrene, and α-methylstyrene. The results are summarized in Table I. The observation that the transient formed from irradiation of DMDAF reacts rapidly with olefins to form cyclopropanes is further evidence that it is the carbene and not the radical or the cation.

The stereochemical outcome of carbene cyclopropanation reactions has often been used to diagnose the spin multiplicity of the reacting carbene.[13,14] We examined the reaction of DMFL with (*E*)-β-deuterio-α-methylstyrene in this regard. Irradiation of the diazo compound in benzene containing 1.8 M olefin gives the expected cyclopropane with complete retention of stereochemistry. This is in contrast to our findings for boraanthrylidene where the analogous reaction is totally nonstereospecific,[2a] and FL where 49% retention of configuration is observed.[1d] Stereospecific cyclopropanation has long been associated with the reaction of singlet carbenes and the nonstereospecific outcome with that of triplets. Thus this result also points to assignment of the detected transient product as ^{1}DMFL.

A competition experiment was performed to confirm that the reactions of the transient species we monitor by laser spectroscopy correspond to the processes leading to the observed products.

Irradiation of DMDAF in benzene containing 0.3 M α-methylstyrene and 0.03 M methyl alcohol is expected, based on the laser kinetics, to give a ratio of ether **1** to cyclopropane of 4.3. The ratio of these two products actually formed was determined by ^{1}H NMR spectroscopy to be within experimental error of the calculated value.

(5) Triplet Sensitization of DMDAF. Triplet sensitization of DMDAF is expected to lead to formation of ^{3}DMFL without first forming the singlet carbene. If the singlet carbene is the ground state, and if intersystem crossing from the first formed triplet is faster than the bimolecular trapping reactions of this state, then sensitization should lead to precisely the same chemical outcome as does direct irradiation. We chose 2,3-benzofluorenone as a triplet sensitizer. The triplet state of this ketone is quenched at approximately the diffusion-controlled rate by DMDAF, but it is quenched by α-methylstyrene with a rate constant of only 1.5 $\times 10^7$ M^{-1} s^{-1}. Moreover, irradiation of solutions containing both benzlfluorenone and DMDAF at wavelengths greater than 400 nm puts the light almost exclusively into the ketone.

We examined the triplet-sensitized reaction of DMDAF with methanol, deuterated α-methylstyrene, and with C_6H_{12}. Within our ability to analyze the product mixtures, the chemical outcome of the sensitized photolyses is virtually identical with those of the direct irradiations. This finding is powerful evidence that DMFL is reacting almost entirely from its singlet state.

(6) Reaction with O_2. Finally, it has been observed by us and by others that triplet carbenes react with oxygen at approximately the diffusion-limited rate.[1,2] If the detected transient species were the triplet carbene, or DMFLH·, its lifetime should be shortened when it is formed in the presence of oxygen. In fact, the lifetime of the transient is the same within our ability to measure it in oxygen-saturated benzene as it is when the oxygen is removed by purging the solution with argon.

Discussion

The major objectives of this work were to elucidate the chemical and physical properties of dimethoxyflurenylidene, to interpret the effect of the substitutes, and to relate the properties of this carbene to those of others that have been studied. These goals have been accomplished to a reasonable degree.

The chemical and physical properties of DMFL are revealed most sharply in contrast with those of FL. This comparison is most apt because the geometrical features, in particular the carbene carbon bond angle, of these two carbenes are expected to be identical. Thus, the differences between DMFL and FL are interpreted solely on the basis of the electronic effect of the substituents.
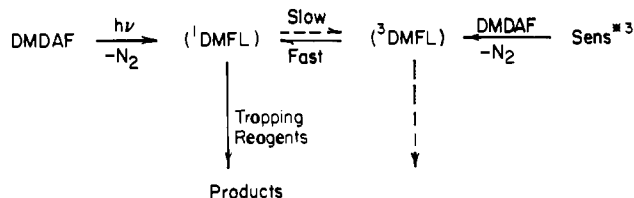
The most profound difference between FL and DMFL is that the spin multiplicities of the lowest electronic states appear to have been inverted. The ground state of DMFL appears to be a singlet. This conclusion is supported by the series of spectroscopic, kinetic, and chemical results presented above. In particular, the absence of an EPR signal characteristic of the triplet carbene, the reaction with alcohols at or very near the diffusion-limited rate, the totally stereospecific cyclopropanation of α-methylstyrene in direct and triplet-sensitized reactions, and the dominant direct insertion into the carbon–hydrogen bond of cyclohexane all indicate little or no contribution from the triplet carbene. On this basis, we assign the absorption spectra shown in Figure 1 to ground-state ^{1}DMFL.

It is interesting to compare the absorption spectrum of FL with that of DMFL. It has been concluded,[1] after considerable uncertainty,[15] that FL exhibits two bands in the visible spectral region; a strong absorption at 470 nm, and a weaker transition at ca. 440 nm. These absorptions are believed to be due to the ground-state triplet. DMFL also exhibits two absorption bands. However, these bands are found to the blue of those for FL, and

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Scheme I

DMDAF $\xrightarrow[-N_2]{h\nu}$ (^{1}DMFL) $\overset{\text{Slow}}{\underset{\text{Fast}}{\rightleftarrows}}$ (^{3}DMFL) $\xrightarrow[-N_2]{\text{DMDAF}}$ Sens^{*3}

Tropping Reagents

Products

they appear to have smaller extinction coefficients. We associate these spectral changes with the differences in spin and electronic configuration of these two carbenes.

It is of some interest to attempt to assign a value to the energy difference between the ground-state singlet and the excited triplet of DMFL. Unfortunately, with the data presently in hand, this cannot be done except in a qualitative way. The chemical properties of FL and diphenylcarbene[1,2] reflect the fact that equilibration between their spin states is more rapid than some bimolecular trapping reactions. Our findings for DMFL indicate that the triplet carbene is present in such small amount that it hardly contributes to the chemistry of this carbene. On this basis, and with the assumption that ^{3}DMFL will have reactivity similar to that of triplet boraanthrylidene,[2a] we feel that this case is at least 2 kcal/mol below the triplet ($\Delta G_{st} \le -2$ kcal/mol). These conclusions are illustrated in Scheme I.

The effect of substituents on aromatic carbenes has been examined by Humphreys and Arnold[4] for diphenylmethylenes. They observe in particular that 4,4'-methoxy substituents do not reverse the normal-state order of triplet below singlet. The more dramatic effect for DMFL is likely to be a consequence of both the smaller energy diference in the parent carbene and a more powerful substituent effect due to the more nearly planar structure of the fluorenyl nucleus.

The effect of the methoxy substiuents on the carbene spin states can be readily anticipated from the theory advanced by Gleiter and Hoffmann.[18] The perturbation of the nonbonding p-type orbital on the carbene carbon by interaction with the occupied orbitals of the fluorenyl residue is expected to be greater for DMFL than it is for FL. The greater perturbation raises the energy of the carbene LUMO, increasing the energy difference between the σ and p carbene orbitals which in turn lowers the value of ΔG_{st}. These concepts are presented more fully in the following paper in this issue.

Experimental Section

General. Proton magnetic resonance (^{1}H NMR) spectra were recorded on Varian Assoc. EM-390 (90 MHz) or XL-200 (200 MHz, FT) spectrometers in deuteriochloroform with tetramethylsilane as an internal standard. Mass spectra (MS) were obtained with a Varian MAT CH-5 and 731 mass spectrometers. Steady-state ultraviolet–visible (UV–vis) absorption spectra was recorded by using a Perkin-Elmer Model 552 spectrometer. Electron spin resonance (EPR) spectra were recorded by using a Varian E-4, X-band instrument with a liquid nitrogen Dewar insert.

2-(2,4-Dimethoxyphenyl)-4,4-dimethyl-2-oxazoline (7). The preparation of this compound closely followed the procedure described by Meyers and co-workers.[19] The reaction of 2,4-dimethoxybenzoic acid (42.2 g, 0.23 mol) with thionyl chloride (82.0 g, 0.69 mol) gave 43.3 g (93%) of the acid chloride. The acid chloride (43 g, 0.22 mol) was combined with 2-amino-2-methyl-1-propanol (35.5 g, 0.43 mol) to form the amide in essentially quantitative yield. The amide (56 g, 0.22 mol) was added to thionyl chloride (77 g, 0.65 mol), and 38 g (76%) of the oxazoline was isolated after vacuum distillation, bp 130 °C (0.07 mm).

2-[2-(3-Methoxyphenyl)-2-(4-methoxyphenyl)]-4,4-dimethyl-2-oxazoline (8). The preparation of this compound was modeled after similar reactions described by Meyers and co-workers.[19] Magnesium (5.0 g, 0.21 mol) was placed in a 250-mL flask and covered with 25 mL of anhydrous

THF. An addition funnel was charged with a solution of 3-bromoanisole (37.4 g, 0.2 mol) in 110 mL of THF. A 20-mL portion of the anisole solution was added to the magnesium in one portion and the mixture began to bubble after a few minutes of stirring. The remainder of the bromoanisole solution was added dropwise, and the mixture was heated at reflux for 12 h.

A solution of **7** (38.3 g, 0.16 mol) in 150 mL of THF was prepared in a 500-mL flask equipped with an addition funnel and a magnetic stirrer. The solution of 3-methoxyphenylmagnesium bromide described above was transferred slowly (24 h) under nitrogen pressure at room temperature into the solution of **7**. The reaction mixture was quenched with 300 mL of saturated aqueous ammonium chloride. The organic layer was removed, and the aqueous layer was washed 3 times with 80-mL portions of ether. The combined organic layers were washed with 50 mL of water and dried with MgSO$_4$, and the solvents were removed under reduced pressure. The crude product was chromatographed on silica gel with a 1:1 mixture of hexane and ethyl acetate to give 40.1 g (79%) of **8**. An analytical sample was prepared by recrystallization from pentane: mp 67.0–67.4 °C, ^{1}H NMR (CDCl$_3$) δ 1.27 (s, 6 H), 3.72 (s, 2 H), 3.78 (s, 3 H), 3.81 (s, 3 H), 6.75–7.70 (m, 6 H); mass spectrum (70 eV), m/e (rel abundance) 310 (100), 225 (22), 255 (11), 296 (9); molecular ion calcd for C$_{19}$H$_{20}$NO$_3$, m/e 310.1443, found 310.1442.

2-(3-Methoxyphenyl)-4-methoxybenzoic Acid (9). Iodomethane (34.7 g, 0.24 mol) was added to **8** (40.1 g, 0.13 mol) in a 250-mL flask. The mixture was stirred at room temperature for 3 h, and then the excess iodomethane was removed under vacuum. The methiodide salt was dissolved in 400 mL of methyl alcohol, and then 400 mL of 20% aqueous NaOH was added and the mixture was heated at reflux for 24 h. The reaction mixture was washed with 100 mL of ether, acidified to pH 2 with 9 N HCl, and extracted 4 times with 100-mL portions of ether. The combined ether extracts were dried with MgSO$_4$, and the ether was removed under reduced pressure. The resulting crude solid was recrystallized from ethanol to give, in two crops, 26.2 g (78%) of **9**: mp 130–131 °C [lit.[20] 134 °C]; ^{1}H NMR (CDCl$_3$) δ 3.80 (s, 3 .H), 3.85 (s, 3 H), 6.77–7.37 (m, 5 H), 7.93 (d, J = 9 Hz, 1 H); mass spectrum (10 eV), m/e (rel abundance), 258 (1), 214 (100), 200 (6); molecular ion calcd for C$_{15}$H$_{14}$O$_4$, m/e 258.0894, found 258.0896.

3,6-Dimethoxy-9-fluorenone (3). A finely ground portion of acid **9** (24.1 g, 0.093 mol) was placed in a flask equipped with a mechanical stirrer. Poly(phosphoric acid) (300 mL) was added to the flask, and the mixture was stirred for 3 h at room temperature. The dark slurry was poured into 500 mL of iced water, and the yellow precipitate that formed was extracted 4 times with 80-mL portions of CHCl$_3$. The combined chloroform extracts were washed with 50 mL of cold water and twice with 50-mL portions of saturated ammonium chloride, dried with MgSO$_4$, and evaporated to give a crude yellow solid. The solid was dissolved in hot ethanol, and upon cooling, long yellow needles of **3** appeared: 12.4 g (55%), mp 142–144 °C [lit.[21] 146 °C]; ^{1}H NMR (CDCl$_3$) δ 3.94 (s, 6 H), 6.65 (d of d J_1 = 8, J_2 = 2 Hz, 2H), 6.89 (d, J = 2 Hz, 2 H), 7.50 (d, J = 8 Hz, 2 H); mass spectrum (70 eV), m/e (rel abundance) 240 (100), 197 (26), 169 (35), 126 (21). The mother liquor contains 1,6-dimethoxy-9-fluorenone.

3,6-Dimethoxy-9-fluorenone Hydrazone (10). A solution of ketone **3** (2.0 g, 8.3 mmol) was prepared in 50 mL of hot ethanol containing 4 mL of 85% hydrazine hydrate. The solution was heated at reflux under a N$_2$ atmosphere for 14 h during which time a yellow precipiate formed. the solid was recrystallized from 1 L of ethanol to give 1.9 g (90%) of hydrazone **10**: mp 202–203 °C; ^{1}H NMR (CDCl$_3$) δ 3.90 (s, 3 H)8 3.94 (s, 3 H), 6.03–6.13 (s, 2 H), 6.73–7.90 (m, 6 H).

3,6-Dimethoxy-9-diazofluorene (DMDAF). A solution of hydrazone **10** (430 mg, 1.7 mmol) was prepared in 100 mL of anhydrous THF. Throughly pulverized mercuric oxide (1.5 g, 6.9 mmol) and anhydrous Na$_2$SO$_4$ (0.7 g) were added to the solution followed by ca. 10 drops of a 10% ethanolic KOH solution. The mixture was stirred under N$_2$ for 12 h at room temperature and then gravity-filtered. The filtrate was evaporated under reduced pressure, and the crude red solid was dissolved in 250 mL of ether. The ether solution was washed with 20 mL of water and dried with MgSO$_4$ and the MgSO$_4$ was removed from the solution and the volume reduced until it became cloudy. Crystallization at −20 °C gave DMDAF 190 mg (44%): mp 240 °C (dec); ^{1}H NMR (CDCl$_3$) δ 3.87 (s, 6 H), 6.93 (d of d, J_1 = 8, J_2 = 2 Hz, 2 H), 7.23 (d, J = 8 Z, 2 H), 7.38 (d, J = 2 Hz, 2 H). Anal. Calcd for C$_{15}$H$_{12}$N$_2$O$_2$: C, 71.42; H, 4.76; N, 11.10. Found: C, 71.33; H, 4.84; N, 10.82.

Low-Temperature EPR Spectroscopy. A 2.3 × 10^{-4} M solution of DMDAF in 2-methyltetrahydrofuran was placed in a quartz EPR tube and immersed in a long-stemmed quartz Dewar which fits into the cavity

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Table II. GC–MS Analysis of Product Mixture from Photolysis of DMDAF in Cyclohexane

retention time,[a] min	m/e[b]	% area[c]	structure
9.02	226	1.6	**2**
10.75	240	7.1	**3**
13.24	308	86	**4**
17.98	450	2.3	**5**

[a]SE-30 5%, 6 ft × $^1/_4$ in. Column temperature program 3 min at 180 °C then 20 °C/min to 290 °C. [b]Nominal mass of the apparent molecular ion. [c]The areas are not corrected for FID response.

of the EPR spectrometer. The sample was irradiated for 1 min at 77 K with a high-pressure mercury arc lamp. A light-purple color was observed in the glass after irradiation. The X-band EPR spectrum was then scanned form zero field to 10 000 G. The experiment was repeated using by 2.3 × 10^{-3} M DMDAF and irradition times up to 10 min. The purple color fades within a few seconds of removing the tube from the Dewar.

A similar experiment was performed by using 2 × 10^{-2} M DMDAF in a Fluorolube matrix. No triplet carbene signals were detected. A control experiment with DAF under the same conditions gives strong signals due to triplet fluorenylidene.

Low-Temperature UV–Vis Spectra. A 2.3 × 10^{-4} M solution of DMDAF in 2-methyltetrahydrofuran was placed in a 1.0-cm quartz fluorescence cell and immersed in a liquid nitrogen-filled Dewar flask equipped with qartz windows. An absorption spectrum of DMDAF in the frozen glass was recorded before irradiation. The sample was irradiated for 1.0 min with a 250-W high-pressure mercury arc lamp while in the Dewar. The spectrum shown in Figure 1A was then recorded.

Laser Flash Photolysis. The laser flash photolysis apparatus has been described previously.[9] A nitrogen laser was used for excitation (337 nm). Concentrations were adjusted so that the sample absorbed a significant portion of the laser light (ca. 6 × 10^{-4} M). Solutions were placed in a 1.0-cm quartz fluorescence cell equipped with a stir bar and Teflon stopcock. Oxygen was removed by purging the solution with dry argon for 5 min. For kinetic measurements, a suitable concentration range of trapping reagents (Table I) were added. The pseudo-first-order rate constants (k_{obsd}) for the decay of the transient at 425 nm was determined by a computer least-squares fit.

Irradiation of DMDAF in Benzene/Methanol. A solution of DMDAF (25 mg, 0.10 mmol) in benzene (24 mL) and methanol (1 mL) was purged with dry N_2 and irradiated in a Rayonet photoreactor equipped with 350-nm lamps for 2 h. At the end of the irradiation period, the UV spectrum of the mixture revealed that all the diazo compound was consumed. Analysis of the photolysis solution by gas chromatography (6 ft × $^1/_4$ in SE-30) initially at 180 °C programmed to 290 °C at 20 °C/min showed three major volatile components with retention times of 9.40, 10.0, and 11.1 min. The three components were isolated by preparative thick-layer chromatography and shown to be 3,6-dimethoxyfluorene (9.40 min), ether **1** (10.0 min), and ketone **3** (11.1 min). The yield of **1** was determined by ^{1}H NMR spectroscopy to be 68%: ^{1}H NMR (CDCl₃) δ 3.00 (s, 3 H)8 3.87 (s, 6 H), 5.44 (s, 1 H), 6.78 (d of d, J_1 = 8, J_2 = 2 Hz, 2 H), 7.10 (d, J = 2 Hz, 2 H), 7.42 (d, J = 8 Hz); mass spectrum (10 eV), m/e (rel abundance) 256 (48), 225 (100); molecular ion calcd for $C_{16}H_{16}O_3$, m/e 256.1099, found 256.1103.

Irradiation of DMDAF in Cyclohexane. A solution of DMDAF (30 mg, 0.12 mmol) was prepared in 90 mL of cyclohexane. The solution was purged with N_2 and then irradiated in a Rayonet reactor with 350-nm lamps for 1 h after which the UV absorption of DMDAF had mostly disappeared. The solvent was removed under vacuum, and the ^{1}H NMR spectrum of the residue revealed 9-cyclohexyl-3,6-dimethoxyfluorene (**4**) in at least 86% yield: ^{1}H NMR (CDCl₃) δ 0.9–1.8 (m, 11 H), 3.71 (d, J = 3 Hz, 1 H), 3.86 (s, 6 H), 6.78 (d of d, J_1 = 8, J_2 = 2 Hz, 2 H), 7.17 (d, J = 3. Hz, 2 H), 7.34 (d, J = 8 Hz, 2 H); mass spectrum (10 eV), m/e (rel abundance) 308 (21)8 225 (100); molecular ion clacd for $C_{21}H_{24}O_2$, m/e 308.1776, found 308.1771. The photolysis mixture was analyzed by GC–MS. The results are presented in Table II.

Irradiation of DMDAF in Benzene-Containing α-Methylstyrene. A solution of DMDAF (30 mg, 0.11 mmol) was prepared in 23 mL of benzene and 3.25 mL of α-methylstyrene (1 M). The solution was purged with N_2 and then irradiated in a Rayonet with 350-nm lamps for 2 h after which time the UV absorption of DMDAF at 375 nm had mostly disappeared. The solvent and remaining α-methylstyrene were removed under vacuum. Analysis of the residue by ^{1}H NMR spectroscopy reveals formation of the expected cyclopropane in ca. 63% yield. The cyclopropane was isolated by preparative thick-layer chromatography: mp 154–156 °C; ^{1}H NMR (CDCl₃) δ 1.72 (s, 3 H), 1.89 (d, J = 5 Hz, 1 H), 2.22 (d, J = 5 Hz, 1 H), 3.77 (s, 3 H), 3.90 (s, 3 H), 5.62 (d, J = 8 Hz, 1 H), 6.31 (d of d, J_1 = J_2 = 2 Hz, 1 H), 6.83 (d of d,

J_1 = 8, J_2 = 8 Hz, 1 H) 7.0–7.5 (m, 8 H); mass spectrum (10 eV), m/e (rel abundance) 342(100), 327(93), 225(10). Molecular ion calcd for $C_{24}H_{22}O_2$, m/e 342.1619; found 342.1612.

In a related experiment (E)-β-deuterio-α-methylstyrene[22] was used. Analysis of the ^{1}H NMR spectrum in this case reveals that the doublet at δ 1.89 has been reduced in intensity. Calculations from the known deuterium content of the styrene indicate that the cyclopropanation is 100% stereospecific.

In a similar experiment, styrene was cyclopropanated to give **6** in very high yield: ^{1}H NMR (CDCl₃) δ 2.05 (d, J = 9 Hz, 2 H), 3.50 (t, J = 9 Hz, 1 H), 3.77 (s, 3 H), 3.87 (s, 3 H) 5.98 (d, J = 9 Hz, 1 H), 6.42 (d of d, J_1 = 9, J_2 = 2 Hz, 1 H), 6.6–7.3 (m, 9 H).

Methanol/α-Methylstyrene Competition. DMDAF (24 mg, 0.095 mmol) was dissolved in benzene containing 0.03 M methanol and 0.3 M α-methylstyrene. The solution was purged with dry N_2 and irradiated in a Rayonet photoreactor equipped with 350-nm lamps for 1 h. The solvent and the remaining methanol and α-methylstyrene were removed under vacuum. The product mixture was analyzed by ^{1}H NMR spectroscopy. The ratio of the methyl ether (**1**) to the cyclopropane was determined by integration of the methyl group singlets at δ 3.00 and 1.72 to be 4.3 ± 0.2.

Triplet-Sensitized Irradiation of DMDAF in the Presence of Methanol. Two samples were prepared in benzene containing 1.0 M methyl alcohol. Both contained 2,3-benzofluorenone (0.02 M) and DMDAF (3.4 × 10^{-3} M). Anthracene (1.6 × 10^{-2} M) was added to one sample as a photochemical control. The samples were placed in test tubes fitted with Teflon stopcocks and magnetic stir bars, purged with dry nitrogen and then irradiated (>400 nm) through a Corning 3-74 filter with a focused high-pressure mercury arc lamp. Under these conditions >85% of the light is absorbed by the 2,3-benzofluorenone. The disappearance of DMDAF was followed by FT-IR (diazo band at 2054 cm⁻¹). After 30 min of irradiation, 53% of the DMDAF had reacted in the sensitized sample. In the sample containing anthracene, only 26% of the diazo compound had reacted. The 2,3-benzofluorenone-sensitized decomposition of DMDAF gave an 86% yield of ether **1** as determined by ^{1}H NMR spectroscopy with toluene as the internal standard.

Triplet-Sensitized Irradiation of DMDAF in the Presence of (E)-β-Deuterio-α-methylstyrene. A solution was prepared containing DMDAF (1.8 × 10^{-3} M), 2,3-benzofluorenne (9.1 × 10^{-3} M), and (E)-β-deuterio-α-methylstyrene (0.25 M) in benzene (25 mL). The solution was purged with dry nitrogen and then irradiated (>400 nm) through a Corning 3-74 filter with a focused high-pressure mercury arc lamp. After 1.0 h of irradition, the benzene was removed under vacuum. The ^{1}H NMR of the remaining unreacted (E)-β-deuterio-α-methylstyrene shows that no isomerization of the olefin had occurred. After evaporation of the styrene at 0.05 torr, only the sensitizer and crude cyclopropane remained. This mixture was analyzed by ^{1}H NMR spectroscopy. The doublet at δ 1.89 was reduced in intensity. Calculations from the known deuterium content of the styrene indicate that the cyclopropanation reaction occurs with complete retention of stereochemistry.

Irradiation of DMDAF in a 1:1 Mixture of Cyclohexane-d_{12} and Cyclohexane-H_{12}. Three deoxygenated samples of DMDAF (3 mg, 0.012 mmol) in 3 mL of C_6H_{12}, C_6D_{12}, and a 1:1 mixture of C_6H_{12} and C_6D_{12} were prepared in quartz test tubes equipped with Teflon stopcocks. The samples were irradiated for 70 min in a Rayonet photochemical reactor (350-nm lamps) equipped with a merry-go-round apparatus. The solvent was removed from each sample by bulb-to-bulb distillation, and the products were analyzed by mass spectroscopy (FI). No increase in the relative abundance of products arising from crossover (m/e 309, 319) was observed from the sample which contained the C_6H_{12}/C_6D_{12} mixture.

Triplet-Sensitized Decomposition of DMDAF in Cyclohexane. A deoxygenated cyclohexane solution of 2,3-benzofluorenone (4.8 × 10^{-3} M) and 1.0 × 10^{-3} M DMDAF was prepared and irradiated for 1.0 h through a Corning 3-74 (400 nm) cutoff filter with a 200-W high-pressure mercury arc lamp. Under these conditions, nearly all the light is absorbed by the 2,3-benzofluorenone. The cyclohexane was removed under vacuum. The major product of this reaction was the cyclohexane insertion product (**4**). The yields of radical coupling and disproportion products **2** and **5** did not increase as a result of triplet sensitization when compared with the direct irradiation of DMDAF in cyclohexane.

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2,4-$(MeO)_2C_6H_3CO_2H$, 91-52-1; 2,4-$(MeO)_2C_6H_3COCl$, 39828-35-8; $(CH_3)_2CNH_2CH_2OH$, 124-68-5; 2,4-$(MeO)_2C_6H_3CONHC$-$(CH_3)_2CH_2OH$, 96617-37-7; *m*-BrC_6H_4OMe, 2398-37-0; (*E*)-PhC-(CH_3)=CHD, 69912-51-2; CH_3OD, 1455-13-6; $(CH_3)_3OH$, 75-65-0; $(CH_3)_3CNH_2$, 75-64-9; $(C_2H_5)_3N$, 121-44-8; PhCH=CH_2, 100-42-5;

m-FC_6H_4CH=CH_2, 350-51-6; *p*-$OMeC_6H_4CH$=CH_2, 637-69-4; PhC-(CH_3)=CH_2, 98-83-9; $(CH_3)_2C$=CHCH_3, 513-35-9; 3',6'-dimethoxy-2-methyl-2-phenylspiro[cyclopropane-1,9'-[9*H*]-fluorene], 96617-44-6; *trans*-3-deuterio-3',6'-dimethoxy-2-methyl-2-phenylspiro[cyclopropane-1,9'-[9*H*]-fluorene], 96617-45-7.

Chemical and Physical Properties of 9-Xanthylidene: A Ground-State Singlet Aromatic Carbene

## Stephen C. Lapin and Gary B. Schuster*

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. Received October 15, 1984

Abstract: Irradiation of 9-diazoxanthene (DAX) leads to loss of N_2 and formation of 9-xanthylidene (XA). This carbene was detected at low temperature in a frozen glass and by laser transient absorption spectroscopy. It reacts rapidly with alcohols to form ethers and with styrenes to give cyclopropanes stereospecifically. At room temperature, XA does not react significantly with hydrocarbons, but at elevated temperature, an insertion reaction characteristic of a singlet carbene is observed. Rate constants for these and other reactions are reported. The data show that XA is a ground-state singlet carbene with a triplet state at least 4 kcal/mol above the singlet. This finding is incorporated into a general explanation of aromatic carbene reactivity.

The characterization of the chemical properties of 9-xanthylidene (XA) is fraught with controversy. Reverdy,[1] in a pioneering study, examined the photolysis of 9-diazoxanthene (DAX) under a wide range of conditions. He reports that irradiation at room temperature in saturated hydrocarbon solvents does not give any of the insertion or abstraction–recombination products typical of other carbenes[2] but, instead, forms dixanthyl ether **1** (from traces of water) and the dimeric xanthone azine **2** (by reaction with DAX), eq 1.
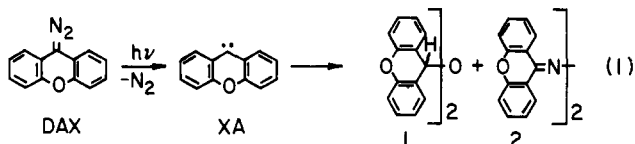
In contrast to the absence of reaction with hydrocarbons, Reverdy[1] found that irradiation of DAX in the presence of alcohols gives excellent yields of the expected ethers, eq 2. Reaction of
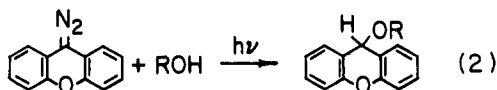
a carbene with an alcohol to give an ether is widely recognized as a reaction characteristic of a singlet-state carbene.[3] However, Reverdy's attempts to add the putative carbene to carbon–carbon double bonds was successful only for the case of styrene. This fact was attributed to participation of triplet xanthylidene (^{3}XA) in this classic cyclopropanation reaction, eq 3.

In a series of papers published subsequent to Reverdy's work, Shechter and co-workers[4] assert that "much of the behavior as-

cribed...to XA is in error". In this study, the subject carbene was
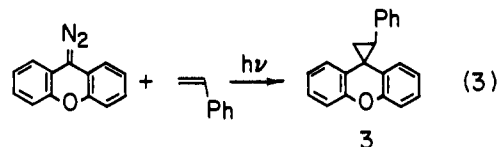
generated by thermolysis of DAX or by photolysis of 9-xanthone tosylhydrazone. These authors report, for example, that addition of DAX to a refluxing sample of cyclooctane (145 °C) does give a good yield of the expected insertion product **4**, eq 4. Also, they
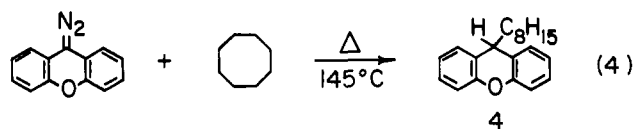
observe that irradiation of the undissolved sodium salt of 9-xanthone tosylhydrazone in neat 2,3-dimethyl-2-butene gives the expected cyclopropane (**5**) in 75% yield, eq 5. These findings
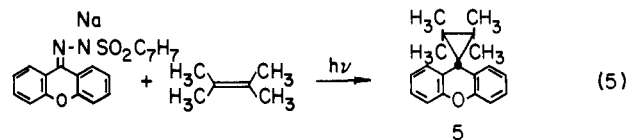
are quite opposite to those reported by Reverdy[1] for photolysis of DAX in the presence of alkanes and alkenes.

Herein we report the results of our investigation of the properties of DAX and XA. The findings permit a rapprochement of the earlier conflicting claims and provide further valuable information on the forces that relate structure to reactivity for aromatic carbenes.

Results

(1) Photolysis of DAX in Frozen Media. Irradiation of a dilute solution of DAX in a methylcyclohexane glass at 77 K creates

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