$2,4\text{-}(MeO)_2C_6H_3CO_2H$, 91-52-1; $2,4\text{-}(MeO)_2C_6H_3COCl$, 39828-35-8; $(CH_3)_2CNH_2CH_2OH$, 124-68-5; $2,4\text{-}(MeO)_2C_6H_3CONHC(CH_3)_2CH_2OH$, 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

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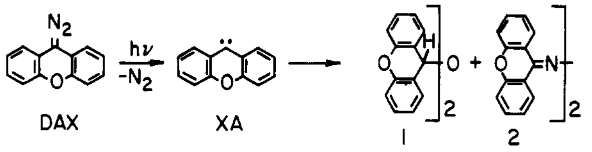
Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. *Received October 15, 1984*

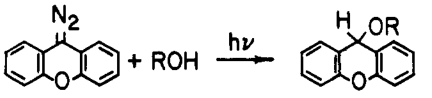
Abstract: Irradiation of 9-diazoxanthene (DAX) leads to loss of N_2 and formation of 9-xanthylidene (XA). This carbene was detected at low temperature in a frozen glass and by laser transient absorption spectroscopy. It reacts rapidly with alcohols to form ethers and with styrenes to give cyclopropanes 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.



(1)

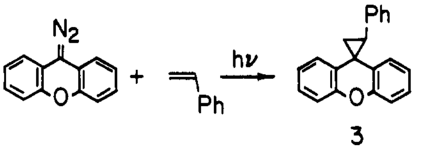
In contrast to the absence of reaction with hydrocarbons, Reverdy[1] found that irradiation of DAX in the presence of alcohols gives excellent yields of the expected ethers, eq 2. Reaction of



(2)

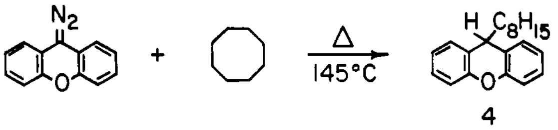
a carbene with an alcohol to give an ether is widely recognized as a reaction characteristic of a singlet-state carbene.[3] However, Reverdy's attempts to add the putative carbene to carbon–carbon double bonds was successful only for the case of styrene. This fact was attributed to participation of triplet 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 ascribed...to XA is in error". In this study, the subject carbene was



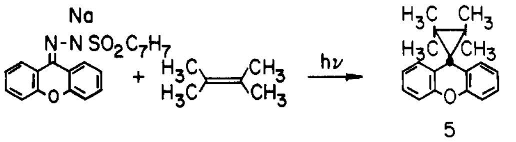
(3)

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



(4)

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



(5)

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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(1) (a) Reverdy, G. *Bull. Soc. Chim. Fr.* **1976**, 1131. (b) *Ibid.* **1976**, 1136. (c) *Ibid.* **1976**, 1141.

(2) (a) Lapin, S. C.; Brauer, B. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 2092. (b) Grasse, P. B.; Brauer, B. E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *Ibid.* **1983**, *105*, 6833. (c) Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *Ibid.* **1984**, *106*, 2227.

(3) (a) Kirmse, W. *Ann. Chem.* **1963**, *666*, 9. Bethell, D.; Stevens, G.; Tickle, P. *J. Chem. Soc. D* **1970**, 792. (b) Tomioka, H.; Miwa, T.; Suzuki, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 753. (c) Zupancic, J. J.; Grasse, P. B.; Lapin, S. C.; Schuster, G. B. *Tetrahedron*, in press. (d) See, however: Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198.

(4) Jones, G. W.; Chang, K. T.; Munjal, R.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 2922. Jones, G. W.; Chang, K. T.; Shechter, H. *Ibid.* **1979**, *101*, 3906.

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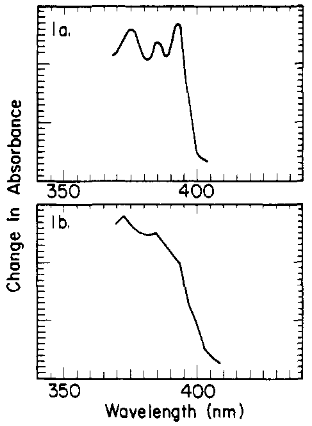


Figure 1. (a) Absorption spectrum obtained by photolysis of DAX in methylcyclohexane at 77 K. (b) Absorption spectrum recorded every 5 nm of transient product 150 ns after pulsed irradiation of DAX in pentane solution at room temperature.

a metastable species. The optical absorption spectrum, Figure 1a, of this species shows three closely spaced maxima at 393, 385, and 376 nm. This spectrum does not change so long as the sample is kept at 77 K, but warming it to room temperature and refreezing results in the disappearance of the metastable species and its replacement by azine **2**. These findings are summarized in eq 6.

The EPR spectra of carbene triplets are quite characteristic and are very useful for revealing their presence in frozen media.[5] Irradiation of DAX at 77 K does not give an EPR spectrum characteristic of ^{3}XA. Instead, only a small amount of a doublet

$$\text{DAX} \xrightarrow[77\text{K}]{h\nu} [393, 385, 376\text{nm}] \xrightarrow[\text{Rt}]{\text{Warm}} \text{Azine 2} \qquad (6)$$

species, presumably xanthenyl radical (XAH·), is observed. Control experiments show that triplet fluorenylidene is easily detected by EPR spectroscopy under these conditions.

It is difficult to reach firm conclusions from the absence of a triplet carbene EPR signal. However, it seems certain that the optical absorptions that are so readily detected at 77 K are not due to ^{3}XA. The observation that warming the glass causes the optically detected species to disappear and azine **2** to appear is consistent with it being XA. This conclusion is supported by the series of spectroscopic and kinetic experiments described below.

(2) Transient Absorption Spectroscopic Analysis of DAX. Irradiation of a 1 × 10^{-3} M solution of DAX in pentane at room temperature with the output of a nitrogen laser (337 nm, 15 ns, 7 mJ) generates a transient species whose absorption spectrum is shown on Figure 1b. This transient product is formed within the 15-ns rise time of the laser, and in dry pentane it decays by a complex kinetic path with a half-life of ca. 50 000 ns. Very similar results are obtained when DAX is irradiated in benzene solution.

The transient absorption spectrum (Figure 1b) exhibits broad maxima at 374, 383, and 393 nm. This spectrum is quite similar to that of the metastable intermediate recorded at 77 K. The only significant changes are those expected to be a consequence of the temperature difference between the samples. For these reasons, we feel that both spectra are due to the same reactive intermediate. The chemical and kinetic properties of this species (described below), in conjunction with the low-temperature spectroscopic results, lead us to conclude that this intermediate is singlet xanthylidene (^{1}XA).

(3) Chemical and Kinetic Properties of ^{1}XA. We confirm Reverdy's observation that irradiation of DAX in a pentane or cyclohexane solution does not give any solvent incorporation products.[1] We isolate, as did Reverdy, good yields of the dimeric products **1** and **2** when DAX is irradiated at low power in a Rayonet photoreactor. The products of this photolysis change when the irradiation is performed with the nitrogen laser as the light source. Under these conditions bis(xanthylidene) (**6**) is a major product, eq 7. The change in products with the change

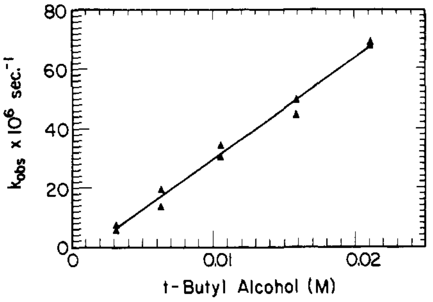
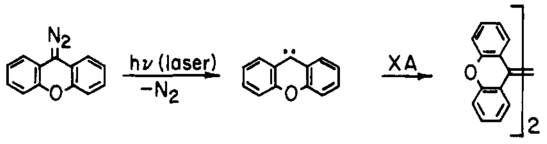


Figure 2. Pseudo-first-order rate constants for the decay of the transient monitored at 390 nm as a function of *tert*-butyl alcohol concentration.

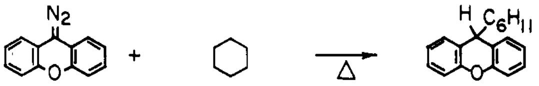


6 (7)

in light source is reasonably due to the ca. 20 000-fold higher concentration of transient XA formed under the laser photolysis conditions. The higher concentration, of course, favors the second-order dimerization to form **6**. This finding helps in the assignment of the transient species detected by laser spectroscopy to ^{1}XA and provides an explanation for the observed complex kinetic behavior of the detected transient product.

The presumed carbene can indeed be forced to react with hydrocarbons at elevated temperature. An important, apparently overlooked, difference between Shechter's experiment that indicates reaction of XA with hydrocarbons[4] and Reverdy's finding that it doesn't[1] is the temperature. We find that thermal decomposition of DAX in cyclohexane at room temperature gives essentially none of the cyclohexane incorporation product (**7**). However, when a 2 × 10^{-2} M solution of DAX in cyclohexane, sealed in a thin-walled glass bulb, is thermolyzed in an oil bath at 200 °C, the solvent incorporation product (**7**) is obtained, eq 8.

Products such as **7** can arise from a direct insertion reaction, characteristic of a singlet carbene, or by an abstraction–recombination sequence associated with the triplet spin state.[6] To



7 (8)

distinguish these possibilities, we thermolyzed DAX in a solvent composed of 50% C_6H_{12} and 50% C_6D_{12}. Analysis of the GC–mass spectrum of **7** formed under these conditions shows no incorporation of deuterium at the 9 position in the compound containing a perhydrocyclohexyl group. This finding indicates that **7** is not formed by an encounter of free cyclohexyl radical with xanthenyl radical. Thus, the interaction of XA with hydrocarbons appears to be primarily that of a singlet rather than a triplet carbene.

Irradiation of DAX in pentane containing *tert*-butyl alcohol gives 9-xanthyl *tert*-butyl ether **8** in high yield, eq 9. The course

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(5) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84*, 4990. Hutchison, C. A., Jr.; Pearson, G. A. *J. Chem. Phys.* **1967**, *47*, 520.

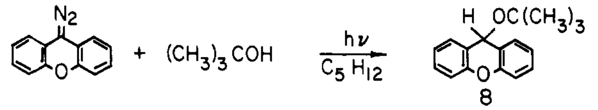
(6) (a) Kirmse, W. "Carbenes", 2nd ed.; Academic Press: New York, 1971. (b) Moss, R. A.; Jones, M., Jr. "Carbenes"; Wiley: New York, 1973; Vol. 1. (c) Jones, M., Jr.; Moss, R. A. "Carbene Chemistry"; Wiley: New York, 1975; Vol. 2. (d) Moss, R. A.; Jones, M., Jr. "Reactive Intermediates"; Wiley: New York, 1978, 1981; Vol. 1, 2. (e) Abramovitch, R. A. "Reactive Intermediates"; Plenum Press: New York, 1980; Vol. 1. (f) Closs, G. L. *Top. Stereochem.* **1968**, *3*, 193.

Table I. Kinetics of Reaction of XA

trapping agent	solvent	rate constant
$(CH_3)_3COH$	pentane	$3.4 \pm 0.3 \times 10^9$ M^{-1} s^{-1}
$(CH_3)_3COH$	cyclohexane	$1.8 \pm 0.1 \times 10^9$ M^{-1} s^{-1}
$(CH_3)_3COD$	cyclohexane	$1.6 \pm 0.2 \times 10^9$ M^{-1} s^{-1}
C_2H_5OH	pentane	$5.1 \pm 0.1 \times 10^9$ M^{-1} s^{-1}
styrene	pentane	$\sim 6 \times 10^{5a}$ M^{-1} s^{-1}
α-methylstyrene	pentane	5.1×10^{6a} M^{-1} s^{-1}
$(C_2H_5)_3N$	pentane	1.4×10^{6a} M^{-1} s^{-1}
DAX	pentane	$\sim 3 \times 10^{7c}$ M^{-1} s^{-1}
$(CH_3)_3COH/N_2$	pentane	3.0×10^{6b} s^{-1}
$(CH_3)_3COH/O_2$	pentane	3.2×10^{6b} s^{-1}

[a] There is some uncertainty in these values because they are small and trace impurities (water, for example) can contribute to the reaction. The true value of these rate constants is no larger than the reported values. [b] These are the observed rate constants for decay of ^1XA in pentane containing 2×10^{-3} M *tert*-buty alcohol either N_2- or O_2-saturated. [c] This value was determined indirectly as described in the text.

of this reaction can be easily observed by using the nanosecond laser techniques we have developed.[2a,b] Photolysis of DAX (1×10^{-3} M) in a pentane solution containing *tert*-butyl alcohol (0–0.02 M) forms the same transient species we detect in the absence of the alcohol. However, in the presence of alcohol, the transient decays following a first-order rate law with a rate constant (k_{obsd}) that depends linearly on the alcohol concentration. A plot of k_{obsd} against the concentration of *tert*-butyl alcohol (Figure 2) is linear, and the slope gives the bimolecular rate constant for reaction of the putative carbene with the alcohol in pentane ($k_{t\text{-BuOH}}^{\text{pentane}}$) equal to 3.4×10^9 M^{-1} s^{-1}. A similar experiment in cyclohexane solution gives a rate constant ($k_{t\text{-BuOH}}^{C_6H_{12}}$) equal to 1.8×10^9 M^{-1} s^{-1}. The difference in the rate constants between these two solvents can easily be traced to their viscosities. This points to a reaction with the alcohol that occurs at or near the diffusion-controlled limit. Further evidence in support of this conclusion comes from the observation that, in contrast to fluorenylidene,[3c] there is no significant kinetic isotope effect when *tert*-butyl alcohol-*d* is used in place of the natural abundance reagent. Finally, the detected transient product reacts 2000 times more slowly with triethylamine than with *tert*-butyl alcohol. The observation of a very rapid reaction with alcohols and a much slower reaction with amines supports the conclusion that the detected transient is ^1XA and not the xanthylium cation.[7] The rate constants for reaction of the carbene with *tert*-butyl alcohol and with other reagents are summarized in Table I.

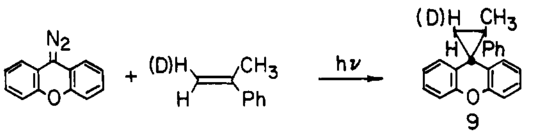


8 (9)

The transient species we have assigned to ^1XA reacts with styrene and a substituted styrene to give the expected cyclopropane. Both Reverdy[1] and Shechter[4] suggest that this is a reaction of the triplet carbene. We studied the kinetics and products of these reactions.

Irradiation of DAX in a pentane solution containing styrene shows that the detected transient intermediate reacts with the olefin. The product of this reaction, which we isolate in ca. 70% yield, is the cyclopropane previously described by Reverdy.[1] The bimolecular rate constant for this reaction ($k_{sty}^{C_6H_{12}}$) is ca. 6×10^5 M^{-1} s^{-1}. This is to be compared with a rate constant for reaction of fluorenylidene with styrene that is ca. 10 000 times greater than this value.[2b,c]

The stereochemistry of the olefin cyclopropanation reaction of carbenes has long been used to identify the spin multiplicity of the reacting state.[8] We used specifically deuterated α-methylstyrene to examine the stereochemistry of this reaction with XA. Irradiation of DAX in pentane containing 0.85 M α-methylstyrene gives the expected cyclopropane, (**9**) eq 10. The ^1H NMR spectrum of this product is quite characteristic. In particular, the two cyclopropyl hydrogens form well-resolved doublets with resonances at δ 1.86 and 2.25. Only one cyclopropane isomer is detected when (E)-β-deuterio-α-methylstyrene is used. This result indicates that the cyclopropanation reaction proceeds with greater than 95% stereospecificity. This behavior is typically associated with singlet carbenes[6,8] and thus again supports our assignment of the transient species as ^1XA.



9 (10)

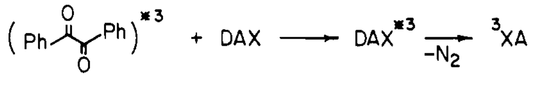
In contrast to the relatively facile reaction with styrenes, we find that the transient carbene we detect does not react significantly with 2,3-dimethyl-2-butene. This finding is exactly consistent with Reverdy's report[1] but, at first glance, appears to conflict with Shechter's results.[4] One clear difference between Shechter's experiment and those done by us and by Reverdy is the source of the carbene. Shechter irradiated a suspension of the sodium salt of 9-xanthone tosylhydrazone which is presumed to form eventually XA. We have examined the reaction of XA with DAX to help explain the different findings.

The dimerization of XA to form **6** under high intensity conditions precludes direct spectroscopic determination of the rate of reaction of XA with DAX. However, an estimate of the rate of this reaction can be obtained from a simple competition experiment. Irradiation of a pentane solution of DAX (6.5×10^{-3} M) containing 0.051 M α-methylstyrene to 15% conversion gives both azine **2** and the expected cyclopropane. From the yields of these products and the measured rate of reaction of XA with the styrene (vide supra), an estimate for the rate constant of reaction of XA with DAX to form **2** (k_{DAX}) of ca. 3×10^7 M^{-1} s^{-1} is indicated.

(4) Triplet Sensitized Reactions of DAX. The results presented thus far seem to indicate clearly that irradiation of DAX leads to the singlet carbene and that the singlet is responsible for all the observed carbene reactivity. We carried out a series of triplet sensitization and trapping reactions in hopes of characterizing the triplet carbene directly.

The phosphorescence of benzil is quenched rapidly by DAX. This reaction leads to the consumption of DAX. Control experiments in which benzil triplet is specifically quenched show that this reaction is due to classical triplet sensitization, eq 11.

Triplet sensitization of DAX in pentane solutions containing *tert*-butyl alcohol or (E)-β-deuterio-α-methylstyrene gives exactly the same results as are obtained by the direct irradiation of DAX.



(11)

That is, ether **8** is formed in the former case and cyclopropanation occurs stereospecifically in the latter. These findings indicate that ^3XA is converted to ^1XA more rapidly than it reacts with either of these bimolecular trapping reagents. These results also support the conclusion that the ground state of XA is the singlet state.

(5) Reaction of XA with O_2. It is of some interest to estimate the energy difference between the singlet and triplet states of XA. This is accomplished by examining the rate of reaction of the detected transient carbene with O_2. We, and others, have found that triplet carbenes react with O_2 at approximately the diffusion-limited rate.[2,6] If there is a small, undetected amount of ^3XA in equilibrium with the lower energy singlet carbene, then the lifetime of ^1XA should be shortened by the presence of O_2. This technique can only yield a limit for estimating the energy difference between the carbene spin states since the rate of reaction of the singlet carbene with O_2 is unknown.

Irradiation of a pentane solution of DAX with the laser in the absence of a trapping reagent leads to complicated reaction kinetics

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(7) Similar aromatic cations react ca. 100 times faster with amines than with alcohols. Sujdak, R. L.; Jones, R. L.; Dorfman, L. M. *J. Am. Chem. Soc.* **1976**, *98*, 4875.

(8) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496.

(vide supra). however, the lifetime of XA does not appear to be affected by the addition of oxygen. In order to quantify these results, we examined the effect of O_2 on XA in pentane containing 2×10^{-3} M *tert*-butyl alcohol. Under these conditions, strict first-order kinetic behavior is observed. The lifetime of XA in O_2-saturated solution is not significantly different from its value in the absence of O_2 (see Table I).

Discussion

The chemical properties of XA are considerably different from those of fluorenylidene (FL) and of boraanthrylidene (BA).[2] Comparisons among these three carbenes as well as with benzofluorenylidene (BFL) and dimethoxyfluorenylidene (DMFL) provide a systematic framework on which to build a rather complete picture of the effect of structure on the chemical and physical properties of carbenes. In this section we first describe our interpretation of the data for XA described above. Next, we attempt to reconcile the apparent contradictory claims for the behavior ascribed to this carbene in previous reports. Finally, we relate the properties of XA to those of other carbenes with the hope of providing an experimentally verified paradigm for the influence of structure on aromatic carbene reactivity.

(1) Chemical and Physical Properties of 9-Xanthylidene. Direct irradiation of DAX certainly leads to the excited singlet state of this diazo compound. Loss of N_2 from this state must generate ^{1}XA. In contrast, triplet-sensitized decomposition of DAX leads to the triplet diazo compound. Loss of N_2 from this triplet state must generate first ^{3}XA. The observation that the chemical outcome is the same whichever DAX multiplicity is probed demands that the communication between spin states must be rapid compared to the bimolecular reactions of this carbene.

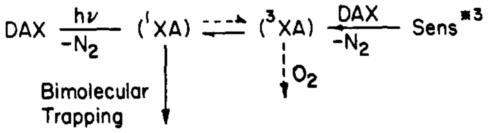
The evidence indicates that the ground state of XA is the singlet. There are two categories of results that support this view. The first is spectroscopic. In particular, the absence of a characteristic EPR spectrum suggests the singlet ground state. The second category is comprised of the set of reactions of XA we have explored.

The reaction of a carbene with an alcohol to form an ether has long been held to be a property characteristic of the singlet spin state.[3] This view has recently been challenged for the case of diphenyl carbene where a direct but slow reaction between this triplet carbene and methyl alcohol is suggested to give the expected ether in a one-step process. The reaction of XA with *tert*-butyl alcohol proceeds at or very near the diffusion-limited rate. This observation quite certainly rules out complications from the proposed spin-forbidden process. Thus, the combination of the spin-specific sensitization results with the kinetic investigation of the reaction with the alcohol points, along with the EPR results, to a single ground state for XA.

Precisely the same conclusion is reached from analysis of the reaction of XA with α-methylstyrene. Stereospecific cyclopropanation has long been a property associated with singlet carbenes.[6,8] Within our ability to detect the alternative isomer, cyclopropanation of this deuterated styrene by XA gives only retained stereochemistry regardless of whether the reaction is initiated by direct irradiation or triplet sensitization of DAX. Thus, the data show that one carbene spin state is responsible for the cyclopropanation reactions, and this state appears to be the singlet.

A reaction that has come to be associated with singlet carbenes is direct insertion into a carbon-hydrogen bond. This is not an important reaction of ^{1}XA at room temperature, but it plays a significant role at higher temperatures. The absence of cross product in the isotope tracer experiment shows that thermolysis of DAX does indeed generate a species capable of inserting into a cyclohexane bond. Evidently, this is a thermally activated reaction that does not compete successfully with other bimolecular reactions of ^{1}XA at room temperature. This is a reasonable consequence of the reduced electrophilicity of ^{1}XA compared with FL, for example. This feature is readily appreciated from the structure of XA and has been anticipated in the work of Reverdy[1] and the calculations of Dürr and co-workers.[10] The reduced electrophilicity also can account for the slow reaction of XA with unactivated olefins.

Scheme I



Finally, we are not able to obtain direct evidence for ^{3}XA in equilibrium with ^{1}XA. The absence of a reaction with O_2, and the assumption of a diffusion-limited rate for reaction of ^{3}XA with O_2, leads to an estimate for the minimum energy difference between ground-state ^{1}XA and excited ^{3}XA (ΔG_{st}) of -4 kcal/mol.

The conclusions expressed above are shown diagramatically in Scheme I. All the observed bimolecular trapping reactions originate with the ground-state singlet carbene. Our attempts to examine ^{3}XA by its reaction with O_2, triplet sensitization of DAX, and the cyclopropanation of deuterated α-methylstyrene all indicate that its concentration in solution is insignificant.

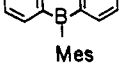
(2) Reconciliation of Previous Apparently Conflicting Claims. As outlined in the introduction, there has been some dispute about the chemical properties properly associated with xanthylidene. Our results indicate that in fact there is no conflict in the claims about the reactivity of XA but that the different behavior is a direct consequence of unappreciated changes in reaction conditions.

To study the reaction of XA with hydrocarbons, Reverdy irradiated DAX at room temperature while Shechter and co-workers pyrolyzed DAX in refluxing cyclooctane. Our findings show that it is the temperature difference between these experiments that accounts for the disparate results. At room temperature, insertion into unactivated hydrocarbons does not compete successfully with the reactions of XA that lead to ether **1** and azine **2**. At elevated temperature, the insertion reaction is competitive. In general, in a set of competing reactions, the one with the higher activation barrier will be accelerated more by increasing temperature. The present case is a good example of this principle.

A conceptually identical explanation can account for the disagreement over the olefin cyclopropanation reaction. Shechter and co-workers in this case presume that they are generating XA by irradiation of the undissolved tosylhydrazone salt of xanthone. Reverdy again generates the carbene by direct irradiation of DAX. Our results reveal a relatively rapid reaction of XA with DAX. This reaction will consume XA before it can undergo a comparatively slow reaction with 2,3-dimethyl-2-butene, for example. Of course, the concentration of DAX in solution is very low when the solid tosylhydrazone salt is used as its source. Thus, the rate of the bimolecular consumption of XA by this route is slowed sufficiently under these conditions to allow the slower reaction with the olefin to proceed.

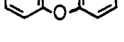
This analysis of the controversy over the chemical properties of ^{1}XA is particularly satisfying since there is no need to abandon any experimental results. The matter is simply resolved by taking full account of the quite different experimental conditions.

(3) Structure and Reactivity of Aromatic Carbenes. A prime objective of our investigation of XA is to illuminate those structural features that control the magnitude of ΔG_{ST} and thereby the chemical properties of aromatic carbenes. In this regard, it is particularly instructive to compare BA and Fl with XAwithin the theoretical framework devised by Gleiter and Hoffmann.[11] Once this has been done, it is a simple matter to include many



BA

FL



XA

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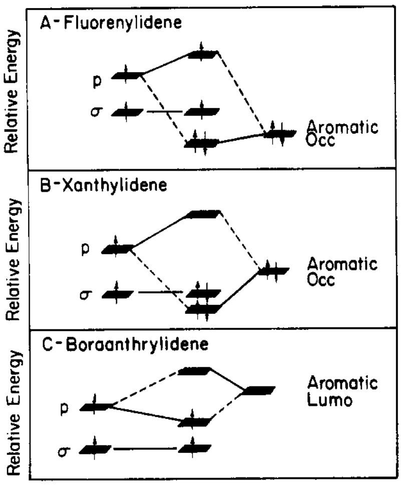

Figure 3. Orbital interactions for (a) FL, (b) XA, and (c) BA.

of the other carbenes that we and others have studied.

Fluorenylidene is a ground-state triplet carbene. However, our findings, and the work of others, indicate that the excited singlet state of this carbene is no more than 1.9 kcal/mol above the triplet.[2] A consequence of the near degeneracy of these two states is their rapid equilibration. Thus, the chemical properties expressed by FL are characteristic of both a singlet and triplet carbene. Boraanthrylidene is also a ground-state triplet carbene. But, in this case, our results show that the singlet is at least 5 kcal/mol above the ground state. This gap is too large to be overcome within the lifetime of the triplet carbene and BA behaves as a classical triplet carbene.[2] The results presented above show that the ground state of XA is the singlet and that the energy of the triplet carbene is at least 4 kcal/mol above the ground state. Thus, the energy gap between the lowest electronically excited state and the ground state of these carbenes spans a range of about 10 kcal/mol with FL located in the approximate center.

A unique feature of carbenes is the existence on one carbon atom of two nonbonding orbitals. One of these is a plane parallel to the carbene carbon and its substituents. This orbital is designated as σ. The second nonbonding orbital is perpendicular to this plane and is designated p. It is important to recognize the effect the relative energy of these two orbitals has on the energy difference between the carbene states.

If these two orbitals have the same or nearly the same energy, then the ground state of the carbene will be a triplet and ΔG_{st} will be large. As the energy difference between the σ and p orbitals increases, the energy of the triplet carbene rises relative to the singlet and the magnitude of ΔG_{st} decreases. Finally, when the energy difference between the σ and p orbitals is larger than that associated with the interaction of two electrons in one orbital, a singlet ground state is predicted for the carbene and ΔG_{st} is negative.[11]

For methylene (CH_2) itself, the triplet is the ground state and ΔG_{st} is ca. 10 kcal/mol.[12] Gleiter and Hoffmann[11] suggested that one way the magnitude of ΔG_{st} can be manipulated is by mixing of the nonbonding carbene p orbital with an occupied or unoccupied orbital of appropriate symmetry. This is shown schematically of FL, BA, and XA in Figure 3.

On the left side of Figure 3A, the two "unmixed" σ and p nonbonding orbitals of a prototypical carbene are shown. The energy difference between these two orbitals is controlled in part by the carbene carbon bond angle. On the right side of Figure 3A, the π-electron orbital array for the fluorenyl residue is represented by an occupied aromatic orbital. Symmetry permits mixing of the nonbonding p orbital, but not the σ orbital. with this aromatic orbital. The result of this mixing is shown for FL in the center of Figure 3A. Note in particular that the energy difference between the singly occupied orbitals in the mixed carbene is greater than it is in the prototype. This leads to the decrease in ΔG_{st}.

Figure 3B depicts the situation for XA. A significant difference between XA and FL is the energy of the aromatic orbital in relation to the nonbonding carbene orbitals. It is expected that the electron-donating ability of oxygen will raise the energy of this orbital and thus increase its mixing with the carbene p orbital. In this case, the splitting of the orbitals in the mixed state is increased sufficiently beyond that of FL to make ΔG_{st} negative. Benzofluorenylidene and dimethoxyfluorenylidene are additional examples of this phenomenon.[9] In the former, ΔG_{st} is ca. half of what it is for FL, and the latter has a singlet ground state. In both cases, the behavior can be understood by considering the relative energy of aromatic electrons.

Finally, Figure 3C displays an analysis of BA. In this case, the orbital chosen to mix with the carbene is the unoccupied aromatic LUMO. We expect that the energy of this orbital is lowered significantly compared to FL by the presence of the vacant atomic orbital of the boron. The singly occupied orbitals of BA are closer in energy than in FL, and thus ΔG_{st} is greater for BA than it is for FL.

The perturbation analysis presented above for the carbenes we have studied is no doubt a gross simplification of reality. In particular, without specific knowledge of the actual energies of the orbitals involved, it is not possible to identify with certainty the important orbital interactions. Nonetheless, these simple concepts seem to provide a valuable framework for interpreting the chemical and physical properties of aromatic carbenes. We are continuing our investigation of these effects.

Experimental Section

General . Proton magnetic resonance (^1H 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.

9-Diazoxanthene (DAX) was prepared according to the procedure described by Holton.[13] A mixture of xanthone hydrazone[14] (0.500 g, 2.40 mmol), dimethylformamide (8 mL), and tetramethylguanidine (2 mL) was stirred under a nitrogen atmosphere at −78 °C. Solid lead tetraacetate (1.3 g, 2.40 mmol, 1.0 equiv) was added in one portion. The mixture turned dark green upon stirring for 30 min at −78 °C. The following workup was performed in a cold room (−15 °C). The diazo compound was extracted into pentane (four 50-mL portions). The combined extracts were washed with two 15-mL portions of 30% KOH and then with two 15-mL portions of water. Dry ice was added to the pentane solution to precipitate tetramethylguanidine as its carbonate. The solution was filtered, and the pentane was removed in a rotary evaporator at 0 °C. The product was dried under a vacuum (0.1 torr) for 1 h at 0 °C to give 399 mg (68%) of light blue-green needles of DAX: mp 60–61 °C dec [lit.[1] 60 °C]. Anal. Calcd for $C_{13}H_8N_2O$: C, 74.99; H, 3.87; N, 13.45. Found: C, 74.87; H, 3.96; N, 12.98.

After several hours at room temperature, the blue-green crystals of DAX turn orange. Recrystallization from benzene gives 9-xanthone azine (**2**): mp 285–287 °C [lit.[1] 289 °C]. DAX was stored in 20–30-mg portions in sealed ampoules under liquid nitrogen. Individual ampoules

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were opened after warming to the temperature of the cold room (−15 °C) and then the appropriate solutions were prepared for spectroscopic or product studies.

Low-Temperature UV–Vis Spectra. A 5.8×10^{-4} M solution of DAX in methylcyclohexane was placed in a 1.0-cm quartz fluorescence cell and immersed in a liquid nitrogen-filled Dewar flask equipped with quartz windows. An absorption spectrum of DAX in the frozen glass was recorded before irradiation. The sample was then irradiated for 2 min with a 250-W high-pressure mercury arc lamp while in the Dewar at 77 K. The spectrum shown in Figure 1a was then recorded.

Low-Temperature EPR. A 5.8×10^{-4} M solution of DAX in methylcyclohexane was placed in a quartz EPR tube and immersed in a long stemmed quartz Dewar which fits into the cavity of the EPR spectrometer. The sample was irradiated for 2 min at 77 K with a high-pressure mercury arc lamp. The X-band EPR spectrum was then scanned from zero field to 10000 G. The experiment was repeated by using DAX concentrations up to 1×10^{-2} M in Fluorolube and methylcyclohexane and irradiation times up to 20 min. Under no conditions was an EPR spectrum characteristic of a triplet carbene observed.

Laser Flash Photolysis. The laser flash photolysis apparatus has been described previously.[15] 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. 1×10^{-3} M for DAX). 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 nitrogen for 5 min.

Photolysis of DAX in a Pentane Solution of α-Methylstyrene. Two samples were prepared; each contained DAX (21.0 mg, 0.10 mmol) dissolved in pentane (25 mL) with α-methylstyrene (0.85 M). One sample was covered with aluminum foil to exclude light. Both samples were cooled to −20 to −25 °C, purged with nitrogen, and irradiated (Rayonet 350-nm lamps). After 25 min, >95% of the DAX absorption band at 362 nm was gone in the uncovered sample. At the same time, <3% of the DAX had reacted in the dark control. Evaporation of the solvent under vacuum at room temperature gave a 54% yield of the cyclopropane in the uncovered sample. This product can be isolated by preparative HPLC by using a 5 × 25 cm 10-μm silica column with chloroform (2%) in hexane as an elutant. The product is a white solid: mp 108–109 °C; ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 3 H, methyl), 1.86 (d, 1 H, cyclopropyl), 2.25 (d, 1 H, cyclopropyl), 6.80 (m, 13 H, aromatic); MS (10 eV), *m/e* (rel abundance) 298 (85), 283 (100), 205 (14), 181 (20); molecular ion calcd for $C_{22}H_{18}O$ *m/e* 298.1358, found 298.1351. In the dark control, **9** was formed in 23% yield. The dark reaction occurs while concentrating the reaction mixture during the workup.

The procedure was repeated by using (E)-α-methyl-β-deuteriostyrene.[16,17] The ^{1}H NMR spectrum was the same as that of the nondeuterated cyclopropane (**9**) except for the cyclopropyl protons: ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 1 H), 1.86 (d, 0.1 H). The resonance at δ 1.86 in this sample was shown to come entirely from residual H in the deuterated styrene.

Triplet-Sensitized Decomposition of DAX. A cyclohexane solution (25 mL) was prepared with 9.5×10^{-3} M benzil and 9.6×10^{-4} M DAX. The solution was cooled to 10 °C and purged with nitrogen for 15 min. The sample was irradiated 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 benzil. A Stern–Volmer analysis shows that DAX is an efficient quencher of benzil phosphorescence ($k_q\tau = 1.6 \times 10^{-5}$ M^{-1}). The cyclohexane was removed under vacuum, and the crude products were analyzed by ^{1}H NMR. No incorporation of cyclohexane was observed in the nonvolatile products.

Triplet-Sensitized Decomposition of DAX in the Presence of *tert*-Butyl Alcohol. A pentane solution (25 mL) was prepared with 9.5×10^{-3} M benzil, 9.8×10^{-4} M DAX, and 0.2 M *tert*-butyl alcohol. The solution was cooled to 0 °C and purged with nitrogen for 15 min. The sample was irradiated for 8 min through a Corning 3-74 (400 nm) cutoff filter with a 200-W high-pressure mercury arc lamp. The pentane and unreacted *tert*-butyl alcohol were removed under vacuum. The ^{1}H NMR spectrum showed a 96% yield of *tert*-butyl 9-xanthanyl ether[1] (*p*-dioxane internal standard). In the absence of benzil, <3% of the DAX is decomposed after 8 min of irradiation under these conditions.

Triplet-Sensitized Decomposition of DAX in the Presence of (E)-α-Methyl-β-deuteriostyrene. A pentane solution (25 mL) was prepared with 0.014 M benzil, 1.02×10^{-3} M DAX, and 1.0 M (E)-α-methyl-β-deuteriostyrene. The solution was cooled to 0 °C and purged with N_2 for 15 min. The sample was irradiated for 8 min through a Corning 3-74 (400 nm) cutoff filter with a 200-W high-pressure mercury arc lamp. The ^{1}H NMR of the unreacted α-methyl-β-deuteriostyrene shows that no isomerization of the olefin occurs under the experimental conditions. Evaporation of the (E)-α-methyl-β-deuteriostyrene in a vacuum gives the expected cyclopropane (**9**) in 63% yield, and the ^{1}H NMR spectrum shows that the cyclopropanation is >95% stereospecific.

Decomposition of DAX in Cyclohexane at Room Temperature. DAX (5 mg, 0.24 mmol) was dissolved in 5.0 mL of cyclohexane in a cell equipped with a Teflon stopcock. The solution was purged with nitrogen for 5 min and left in the dark overnight at room temperature. The cyclohexane was removed under vacuum and the products were analyzed by ^{1}H NMR spectroscopy. The major products were the azine (**2**) and the ether (**1**). No incorporation of cyclohexane in the products was detected.

Thermolysis of DAX in Cyclohexane. DAX (5 mg, 0.024 mmol) was dissolved in cyclohexane (1.2 mL) in a 3-mL thin-walled glass bulb. The solution was degassed by two freeze–pump–thaw cycles. The bulb was then sealed under vacuum and submerged in a 200 °C oil bath. The green color of the DAX was gone in less than 15 s. The crude products were analyzed by ^{1}H NMR and by GC–MS. The major product was 9-xanthone azine (**2**). However, 9-cyclohexylxanthene (**7**) was also formed in 14% yield. The experiment was repeated with an equal molar mixture of cyclohexane and cyclohexane-d_{12}. The GC–MS of **7** shows products corresponding to the incorporation of cyclohexane (*m/e* 264) and cyclohexane-d_{12} (*m/e* 276). No products above a detectable limit of ca. 5% corresponding to a crossover were observed (*m/e* 265, 275).

Products from Steady State and Pulsed Laser Photolysis of DAX in Pentane. DAX (16.3 mg, 0.078 mmol) was dissolved in pentane (25 mL). The solution was cooled to −20 to −25 °C in a dry ice/2-propanol bath, purged with N_2 for 15 min, and irradiated (Rayonet 350 lamps) until 95% of the DAX absorption at 362 nm was gone (10 min). The pentane was removed under vacuum, and the crude products were analyzed by ^{1}H NMR (*p*-dioxane internal standard). The following products were obtained: 9-xanthone azine (**2**) 61%, xanthone 14%, and ether (**1**) 3%. No bixanthylene was detected in the product mixture.

The procedure was repeated by using a nitrogen laser to irradiate the DAX (8.8 Hz, 30 min). The following products were obtained: bixanthylene (**6**) 35%, azine (**2**) 20%, xanthone 16%, and ether (**1**) 4%.

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Registry No. 1, 6538-19-8; **2**, 95952-63-9; **6**, 517-45-3; **7**, 32749-07-8; **8**, 61307-89-9; **9**, 96503-12-7; **9**-d_1, 96503-13-8; DAX, 51933-61-0; $(CH_3)_3COH$, 75-65-0; CH_3COD, 3972-25-6; C_2H_5OH, 64-17-5; $(C_2H_5)_3N$, 121-44-8; xanthone hydrazone, 4132-55-2; α-methylstyrene, 98-83-9; (E)-α-methyl-β-deuteriostyrene, 69912-51-2; cyclohexene, 110-82-7; styrene, 100-42-5.

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