

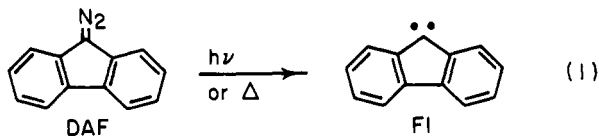
# Chemical and Physical Properties of Fluorenylidene: Equilibration of the Singlet and Triplet Carbenes

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**Abstract:** Irradiation of 9-diazofluorene, with a pulsed laser on a picosecond or nanosecond time scale at room temperature, or at 10 K in a glassy matrix, gives detectable fluorenylidene. This species is shown to exist, under most experimental conditions, as a rapidly equilibrating mixture of singlet and triplet carbenes. The reaction of fluorenylidene with acetonitrile, cyclohexane, and various alcohols and olefins was studied. The products from these reactions and the rates of most of these transformations are reported. Analysis of the kinetic and spectroscopic data shows that singlet fluorenylidene is only ca. 1.1 kcal/mol above ground-state triplet fluorenylidene. The chemical causes and consequences of this small energy gap are discussed.

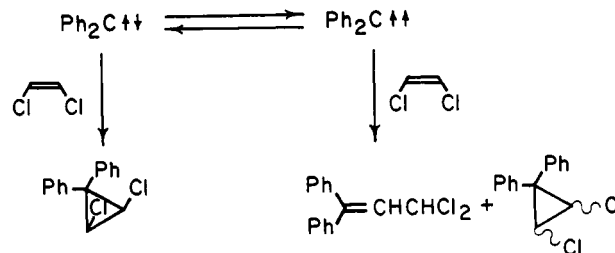
The chemical and physical properties of carbenes have been the focus of considerable attention for well over 40 years. In that period thousands of papers on their reactions, spectroscopy, and structure have been published. Much of this work has been reviewed, and several comprehensive monographs and more sharply focused chapters are available.<sup>1</sup> Our interest has been centered on the properties of fluorenylidene (Fl), a carbene generated either by thermolysis or photolysis of 9-diazofluorene (DAF) (eq 1). Herein we report the results of our chemical and spectrophotometric investigation of this carbene.<sup>2</sup>



Fluorenylidene is an example of a general class referred to as arylcarbenes. In this group one or both of the hydrogen atoms of methylene (CH<sub>2</sub>, the simplest carbene) have been replaced by an aromatic group. The properties of Fl, as we will show below, are closely related to the other carbenes within this class.

One of the most difficult problems encountered in the study of carbenes is the assignment of a particular chemical property to a specific electronic state. The two lowest-lying states of carbenes have different spins. For arylcarbenes, low-temperature EPR spectroscopy has shown conclusively that the ground state is a bent triplet with two orthogonal singly occupied orbitals.<sup>3,4</sup> Analysis of the chemical properties of arylcarbenes reveals that the first excited state is an electrophilic singlet and that the difference in energy between the triplet and singlet states can be quite small. This small energy difference between the lowest states of arylcarbenes exacerbates the difficulties in assigning them specific chemical properties. Under some conditions the rate of equilibration between these lowest states is faster than competing bimolecular reactions of either state. However, it has become clear to us during the investigation of Fl that the existence of this rapid

Scheme I



equilibration condition is a variable that depends on such things as temperature and the nature and concentration of added trapping reagents.

The first experimental evidence suggesting equilibration between singlet and triplet carbenes was uncovered by Bethell and co-workers,<sup>5</sup> who studied the thermal reaction of diphenyldiazomethane in acetonitrile solution. They observed a competition between formation of diphenylmethyl ethyl ether from added ethanol and dimerization to form tetraphenylethylene and benzophenone azine. The reaction of carbenes to form ethers from alcohols had been suggested previously by Kirmse<sup>6</sup> to be a characteristic of singlet carbenes. This conclusion subsequently has been tested numerous times<sup>7-12</sup> and is nearly universally accepted. The observed dimerization reactions, on the other hand, were believed to originate with the ground-state triplet carbene. Kinetic and product analysis of these transformations led Bethell to suggest that reconversion to the singlet state is one of the important reactions of triplet diphenylmethylene. The rapid equilibration of the spin states of this carbene was supported further by the study of its reaction with 2-propanol in acetonitrile.<sup>8</sup> In this case hydrogen atom abstraction, a characteristic reaction of triplet carbenes,<sup>13-16</sup> competes with ether formation. However, a subsequent study<sup>17</sup> of inter- and intramolecular isotope effects on the reaction of diphenylmethylene in acetonitrile with *n*-butyl- and *tert*-butylamine revealed that, with these reagents, the bimolecular reaction of triplet diphenylmethylene is more rapid than

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its reconversion to the singlet state. Under these conditions equilibrium between the spin states is not maintained.

In a pioneering spectroscopic study, Closs and Rabinow<sup>18</sup> examined triplet diphenylmethylene in acetonitrile and in benzene solution following flash photolysis of diphenyldiazomethane. They monitored the rate of reaction of this triplet carbene with itself to form tetraphenylethylene, with methanol to form an ether, and with butadiene to give 2-vinyl-1,1-diphenylcyclopropane. The authors chose to attribute the cyclopropanation reaction specifically to triplet diphenylmethylene and ether formation to the singlet state. However, if the rapid equilibration of carbene spin states is maintained, as it is argued to be, then this assignment cannot be made with absolute certainty. Nevertheless, reasonable interpretation of the kinetic results obtained showed that the energy gap between singlet and triplet diphenylmethylene is no greater than 3 kcal/mol.

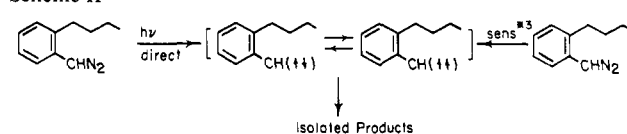
A recent investigation of the direct and sensitized photolysis of diphenyldiazomethane by Eisenthal, Turro and co-workers<sup>19</sup> in acetonitrile solution leads to conclusions similar to those obtained by Closs and Rabinow.<sup>18</sup> In this study, picosecond laser spectrophotometric techniques were employed to reveal a 110-ps rise time for the appearance of the triplet carbene. And the free energy difference between the triplet and lowest singlet state was estimated to be  $5.1 \pm 1$  kcal/mol.

Further evidence for relatively rapid equilibration of the lowest states of diphenylmethylene comes from a recent report by Gaspar and co-workers,<sup>20</sup> who studied the reaction of this carbene with *cis*- and *trans*-1,2-dichloroethylene. It has earlier been suggested<sup>21,22</sup> that the reactions of this olefin might be diagnostic for the spin state of a reacting carbene. With diphenylmethylene, three products containing dichloroethylene were obtained, *cis*-cyclopropane, *trans*-cyclopropane, and 3,3-dichloro-1,1-diphenyl-1-propene, which results from chlorine migration (Scheme I). Neither the stereochemical outcome of the cyclopropanation nor the relative yield of cyclopropanes and rearrangement product was sensitive to dilution with hexafluorobenzene or addition of styrene. Stereospecific cyclopropanation of an olefin has long been a hallmark of the reactions of singlet carbenes.<sup>16,23-25</sup> The authors chose to explain the high degree of stereospecificity observed in this case by postulating predominant addition of the singlet carbene and attribute the nonstereospecific cyclopropane and the rearrangement products to triplet carbene parentage. The insensitivity of these product ratios to hexafluorobenzene, which was believed to enhance triplet carbene formation,<sup>26</sup> and styrene, which is presumed to react rapidly with the triplet carbene, was used to support the conclusion that there is a mobile equilibrium between the lowest states of diphenylmethylene.

The rapid achievement of equilibrium between the triplet and the lowest singlet state of diphenylmethylene is consistent with the sensitivity of the reactions of this carbene to olefin structure observed by Jones and co-workers.<sup>27,28</sup> However, the dependence of the stereochemical outcome of styrene cyclopropanation to dilution with hexafluorobenzene<sup>28</sup> is not consistent with maintenance of a single equilibrium mixture under all reaction conditions.

A second arylcarbene that has received considerable attention is phenylmethylene. Moss and Dolling<sup>16</sup> report that the stereo-

Scheme II



chemical outcome of olefin cyclopropanation by this carbene is unaffected by perfluorinated diluents or by added diene "triplet traps". However, lowering the temperature and forming a frozen matrix decrease the stereospecificity of this reaction. These findings are consistent with the establishment of a temperature-dependent equilibrium mixture of triplet and singlet phenylmethylene states.

Perhaps the most compelling evidence for rapid equilibration of phenylmethylene states is the report of Baer and Gutsche<sup>29</sup> on the direct and sensitized photolysis of (2-*n*-butylphenyl)diazomethane. In this case, photolysis in cyclohexane solution gives a mixture of seven isolated and identified products. The identity and yield of these products are the same whether the reaction is initiated by direct photolysis of the diazo compound, which presumably generates the singlet carbene first, or sensitized decomposition of the diazo compound with triplet benzophenone to give the triplet carbene directly (Scheme II).

In a similar vein, Tomioka and co-workers<sup>30</sup> have recently explored the reactions of phenylmethylene with alcohols following the direct or triplet-sensitized irradiation of the diazo compound. The same ratio of singlet-carbene-derived ether to triplet-carbene-derived hydrogen atom abstraction is obtained regardless of the carbene spin state when it is first created. This ratio is sensitive to temperature, however, which probably reflects both a change in the relative amount of the triplet carbene present in the equilibrium mixture and the increased importance of hydrogen atom tunneling<sup>31</sup> as the rates of other processes decrease.

Although not strictly an arylcarbene, the properties of cyclopentadienylidene have considerable relevance to our investigation of fluorenylidene. EPR spectroscopy reveals that this carbene also has a triplet ground state,<sup>32</sup> and chemical investigations<sup>25,33,34</sup> have shown that many of its reactions originate with the singlet state, which is likely in rapid equilibrium, under most conditions, with the triplet.

If rapid equilibration between the lowest states of arylcarbenes is the rule, it appeared for some time that fluorenylidene is the exception. The unusual properties of this carbene have often been noted.<sup>20,25,27,35</sup> In particular, where diphenylmethylene reacts with substituted olefins mainly by hydrogen atom abstraction, fluorenylidene gives primarily cyclopropanes nonstereospecifically. Also, and most critically, a series of experiments by Jones and Rettig<sup>26,36</sup> seemed to show that, in contrast to diphenylmethylene, reconversion of triplet fluorenylidene (<sup>3</sup>Fl) to the singlet (<sup>1</sup>Fl) does not compete with the bimolecular cyclopropanation of olefins by the ground-state triplet.<sup>20</sup> This conclusion was based on the observations that dilution with then-presumed inert hexafluorobenzene leads to less stereospecific olefin cyclopropanation and that inclusion of butadiene, a presumed specific triplet trap, results in more stereospecific cyclopropanation. These unusual properties of fluorenylidene led us to choose it as a target for investigation first by nanosecond laser spectroscopy and later using picosecond techniques. The results of these, and other, experiments are presented below.

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## Results

**Low-Temperature Spectroscopy.** The EPR spectrum of fluorenylidene has been obtained by Trozzolo and co-workers in a Fluorolube matrix at 77 K.<sup>3</sup> This experiment allows relatively certain assignment of the ground state of this carbene to the triplet. In order to utilize the pulsed-laser spectrophotometric technique, it is necessary to identify the optical absorption spectra of the species of interest. Unfortunately, at the outset of this work little information was available on the optical spectrum of fluorenylidene.

In an early report, Closs and co-workers<sup>37</sup> describe measuring the absorption spectra of diphenylmethylene and of fluorenylidene in a crystalline host at the boiling point of liquid hydrogen. An absorption band for triplet diphenylmethylene with a maximum at ca. 400 nm was observed, and the spectrum of fluorenylidene was reported to be similar to that of diphenylmethylene in several respects.

Trozzolo and Gibbons<sup>38</sup> measured the absorption, emission, and excitation spectra of a series of substituted diphenylcarbene triplets at 77 K in a variety of rigid organic matrices. They observed that the absorption spectra of these compounds consist of two bands, a strong UV absorption with a maximum near 300 nm and a weaker visible band with a maximum near 465 nm.

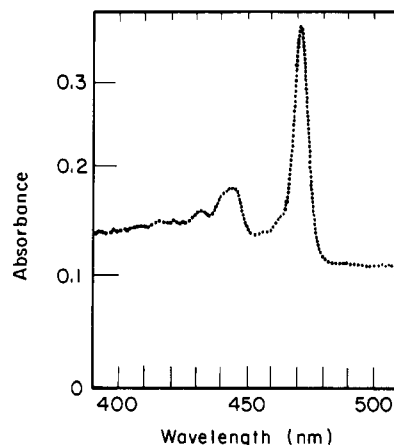
Similarly, Moritani and co-workers<sup>4,39,40</sup> reported measuring the optical and EPR spectra of fluorenylidene analogues dibenzo[*a,d*]cycloheptenyliene (1) and dibenzocyclo-



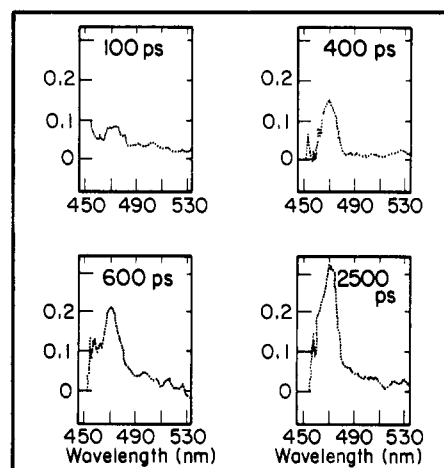
heptadienyliene (2) at 77 K in frozen organic matrices. The EPR spectra of 1 and 2 are persistent under these conditions, indicating both the triplet ground state of these carbenes, and their chemical stability at 77 K. They reported that the optical spectra of these carbenes consist of two bands, a strong UV transition, observed at 380 nm for 1 and at 350 nm for 2, and a weaker visible transition reported at 486 nm for 1 and 500 nm for 2.

The optical spectrum of triplet fluorenylidene is difficult to obtain. EPR spectroscopy reveals that this carbene is stable at 77 K in Fluorolube, but it is not possible to measure the optical spectrum in this material because it freezes and becomes opaque. On the other hand, triplet fluorenylidene is not stable at 77 K in typical glass-forming media. We observed that the EPR spectrum of <sup>3</sup>Fl decayed in a few seconds at 77 K in a methylcyclohexane glass.<sup>31,41</sup> Nevertheless, we attempted to measure the optical spectrum of <sup>3</sup>Fl in this matrix by flash photolysis of DAF and photographic detection of the absorption spectrum ca. 1 s after irradiation. This procedure revealed two absorption bands, a strong UV transition at ca. 390 nm and a weaker visible band. On the basis of this result, the spectra of triplet carbenes reported previously, and the results of some nanosecond laser photolysis experiments to be described below, we assigned these spectral features to triplet fluorenylidene.<sup>2a</sup> Unfortunately, that assignment is incorrect. And, as a consequence, several of the conclusions reached earlier must be revised.

Photolysis of a dilute solution of DAF at ca. 10 K in a 2-methyltetrahydrofuran (MTHF) glass generates <sup>3</sup>Fl, which EPR spectroscopy shows to be stable for at least several hours. The optical absorption spectrum under these conditions is also stable. It consists of two bands, a strong transition at 470 nm and a weaker absorption at ca. 440 nm (Figure 1). Both the EPR signals and these absorption bands disappear when the MTHF matrix is



**Figure 1.** Absorption spectrum obtained after photolysis of DAF at 10 K in a 2-methyltetrahydrofuran glass. Both the band at 440 nm and at 470 nm disappear in a few seconds when the matrix is warmed to 77 K.



**Figure 2.** Absorption spectra recorded after irradiation of DAF in acetonitrile solution at room temperature with a 30-ps light pulse at 355 nm.

warmed from 10 to 77 K. Mindful of the inherent differences in sensitivity between the EPR and optical spectral techniques, we assigned, based on the results described above and picosecond-laser and chemical-trapping experiments presented below, the optical absorption bands observed at 10 K to triplet fluorenylidene. A similar conclusion has been reached by Griller, Scaiano, Platz and co-workers based on different evidence.<sup>42a</sup>

**Pulsed-Laser Spectroscopy.** Two general techniques were employed to obtain spectra of the transient intermediates formed from photolysis of DAF. The first uses a mode-locked Nd-YAG laser and is capable of 30-ps resolution. This apparatus is described in the Experimental Section. The second technique employs a nitrogen laser and provides time resolution of about 13 ns. This equipment has been described previously.<sup>43</sup> We examined the spectral and kinetic consequences of irradiation of DAF in both time regimes in a variety of solvents at room temperature.

The first experiments we carried out were in acetonitrile solution. The work of Bethel<sup>5,7,8,17</sup> and others<sup>18,19,44</sup> seemed to indicate that this solvent is relatively inert toward reaction with singlet and triplet arylcarbenes. This observation does not withstand intensive investigation, and some of the conclusions drawn from the earlier studies in this solvent may require reinterpretation.

Photolysis of DAF in acetonitrile solution with a 30-ps pulse at 355 nm results in the spectral changes shown in Figure 2. At

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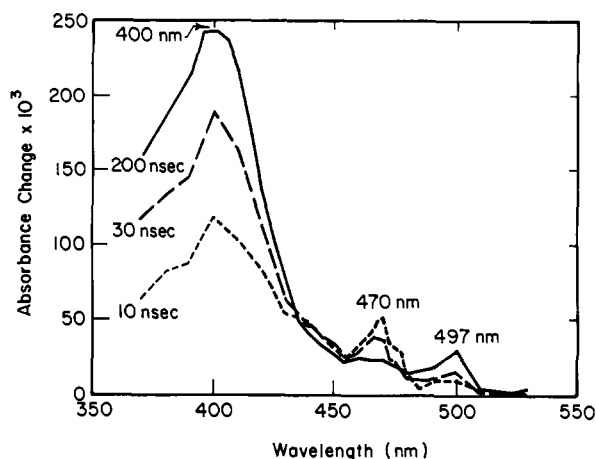
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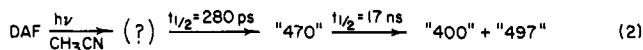


**Figure 3.** Absorption spectra recorded after irradiation of DAF in acetonitrile solution at room temperature with a 13-ns light pulse at 337 nm. The optical density was recorded at ca. 1-nm intervals.

the earliest times, ca. 30 ps after the flash, there is no detectable absorbing transient product in the spectral range we can examine. As time proceeds, however, a species with an absorption maximum at 470 nm begins to appear. The concentration of this species reaches a maximum ca. 1000 ps after the laser pulse, and then, on this time scale, appears to remain constant. Fitting the growth of this absorption to a first-order rate law gives a half-time for its appearance of  $280 \pm 90$  ps.

Irradiation of DAF in acetonitrile solution with a 13-ns pulse at 337 nm also permits observation of the transient product with a maximum at 470 nm. However, on the longer time scale of this experiment, this product is not stable, but is consumed in an apparent first-order process with a half-life of  $17 \pm 2$  ns (Figure 3). Two new features grow into the absorption spectrum at the same rate as the absorption at 470-nm decays. The first has a peak at ca. 400 nm and the second at 497 nm. Both of these absorptions reach a maximum absorbance ca. 100 ns after the laser pulse, and both are constant thereafter for many microseconds. Additional evidence that the transient product responsible for the absorption at 470 nm is the immediate precursor to both the 400- and 497-nm absorbing products derives from isobestic points observed at 433, 457, and 480 nm (Figure 3).

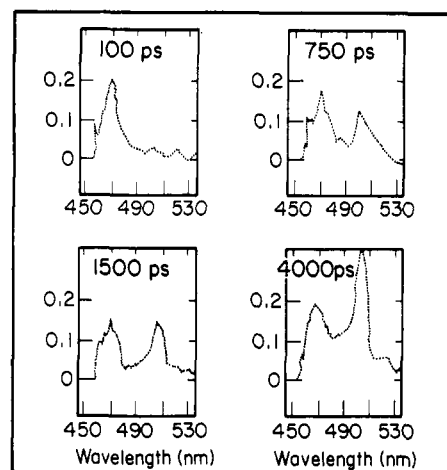
The results of the picosecond and nanosecond laser photolysis of DAF in acetonitrile solution are summarized in eq 2. Ori-



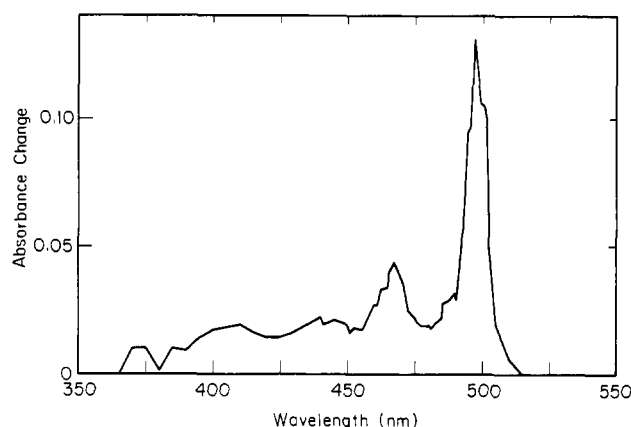
ginally, based on the nanosecond experiments and its reaction with methanol to be described below, we associated the transient product absorbing at 470 nm with  $^1\text{Fl}$  and the 400- and 497-nm absorptions with  $^3\text{Fl}$ . However, the picosecond time scale results, the spectroscopy at 10 K, and chemical sensitization experiments described below clearly demand revision of these assignments.

Photolysis of DAF in cyclohexane solution produces fewer transient products than are observed in acetonitrile. Figure 4 shows spectra recorded following picosecond laser irradiation of DAF in cyclohexane. At early times only the absorbance at 470 nm is present, but as time proceeds, a band at ca. 497 nm appears in the spectrum. The half-time of growth for the 497-nm absorption is  $1400 \pm 600$  ps at room temperature.

On a nanosecond time scale, photolysis of DAF in cyclohexane yields the spectrum shown in Figure 5. We assign the two absorption bands in this spectrum at 470 and 497 nm to the 9-fluorenyl radical (FIH $\cdot$ ). The UV absorptions of FIH $\cdot$  have been reported by Norman and Porter.<sup>45</sup> Scaiano, Griller and co-worker<sup>42b</sup> have obtained an identical spectrum of FIH $\cdot$  from the reaction of *tert*-butoxy radical with fluorene. These findings, and the clear free-radical origins of the eventual stable products (see



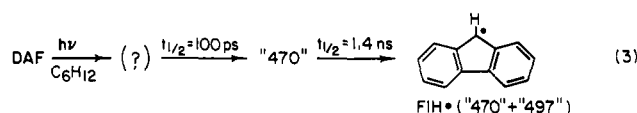
**Figure 4.** Absorption spectra recorded after irradiation of DAF in cyclohexane solution at room temperature with a 30-ps light pulse at 355 nm.



**Figure 5.** Absorption spectrum recorded 100 ns after irradiation of DAF in cyclohexane solution at room temperature with a 13-ns light pulse at 337 nm.

below) of this reaction,<sup>2d,56</sup> support the assignment.

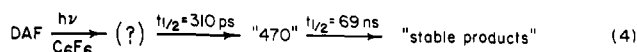
The results of the picosecond and nanosecond laser photolysis of DAF in cyclohexane solution are summarized in eq 3. As in



acetonitrile, and at 10 K, the first transient product detected in cyclohexane solution is the one with an absorbance at 470 nm. This species rapidly abstracts a hydrogen atom from cyclohexane ( $k = 7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) to give FIH $\cdot$ . As shown by Scaiano and co-workers,<sup>42b</sup> the 497-nm absorption observed in acetonitrile solution is also due to formation of FIH $\cdot$ .

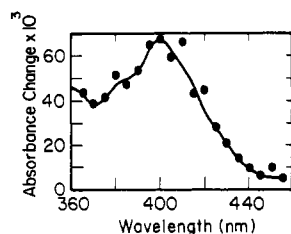
For convenience, some of the experiments described below are carried out in spiro[2.2]pentane solution.<sup>46</sup> The spectroscopic results are qualitatively identical with those obtained in cyclohexane. However, presumably due to the increased strength of the carbon-hydrogen bonds in this solvent, the half-life of the carbene absorbing at 470 nm is increased to  $29 \pm 6$  ns.

The photolysis of DAF in solutions containing hexafluorobenzene has played a pivotal role in the interpretation of the properties of fluorenylidene. Picosecond laser photolysis of DAF in hexafluorobenzene gives the results summarized in eq 4. Again,



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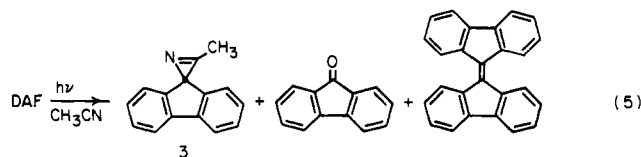


**Figure 6.** Absorption spectrum recorded 150 ns after irradiation of azirine **3** in acetonitrile solution at room temperature with a 20-ns light pulse at 308 nm.

the first transient product observed in this solvent absorbs at 470 nm. As in the other solvents examined, this product is not formed instantaneously but appears following a first-order rate law with a half-time of  $310 \pm 50$  ps. The nanosecond laser experiments reveal that this solvent is not "inert" but that the presumed carbene absorbing at 470 nm is consumed with a half-life of  $69 \pm 4$  ns at room temperature. We have not identified the eventual stable products of this reaction beyond confirming<sup>42a</sup> that a major component has a molecular formula of  $C_{19}H_8F_6$ , which corresponds to the combination of fluorenylidene and hexafluorobenzene. Addition of fluorenylidene to benzene has been observed to form a norcaradiene.<sup>47</sup>

**Chemical and Kinetic Analysis of Product Formation from Photolysis of DAF.** In this section we present first a description of the reactions of fluorenylidene with acetonitrile and with cyclohexane. Then we report the results of the investigation of the reaction of this carbene with varying concentrations of added alcohols and olefinic trapping reagents. These experiments, in conjunction with the low-temperature and laser spectroscopy, clearly reveal the properties of fluorenylidene.

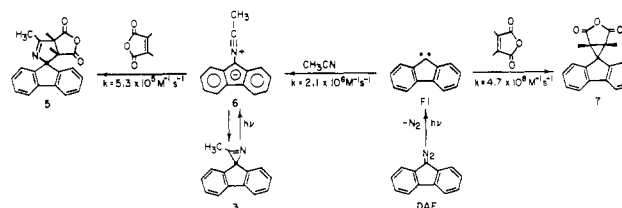
**A. Photolysis in Acetonitrile.** Bethell noted<sup>5</sup> that thermolysis of diphenyldiazomethane in acetonitrile gives a complex mixture of products consisting of dimeric structures and radical coupling products, among other unidentified components. The photolysis of DAF in acetonitrile similarly gives a complex product mixture. From that mixture we have isolated and identified fluorenone, bifluorenylidene, and 2*H*-azirine **3** (eq 5). Griller and co-



workers<sup>42a</sup> report obtaining a gas chromatograph peak from a similar reaction mixture whose mass spectrum is consistent with its being 9-fluorenylacetonitrile. The formation of these products indicates clearly that the carbene formed from photolysis of DAF is reacting with the acetonitrile solvent. We have studied this reaction in some detail.

The photochemistry of 2*H*-azirines has been extensively investigated by Padwa<sup>48a</sup> and by Schmid.<sup>48b</sup> In general, irradiation leads to ring cleavage and formation of a nitrile ylide. Ylide generation from the reaction of carbenes with heteroatomic functional groups is well-known.<sup>49,50</sup> Tomioka and co-workers<sup>10</sup> observed carbonyl ylide formation from diphenylmethylene and benzophenone. Similarly, Scaiano, Griller and co-worker<sup>51a</sup> report ylide formation from fluorenylidene and several ketones. And Huisgen and de March<sup>51b</sup> trapped the ylide formed from benz-

**Scheme III**



aldehyde and (dicarboethoxy)carbene. At the outset of our investigation, there was no indication that arylcarbenes react with nitriles to form ylides. However, there have been several reports<sup>52</sup> implicating nitrile ylides in the reactions of electron-poor carbenes with nitriles.

We prepared azirine **3** by the procedure of Smolinsky and Pryde.<sup>53</sup> Irradiation of this azirine with a 20-ns pulse at 308 nm<sup>54</sup> gives a transient product whose absorption spectrum (Figure 6) shows a maximum at ca. 400 nm. The similarity of this spectrum to the one obtained from the reaction of fluorenylidene with acetonitrile (Figure 3 at 200 ns) suggests that a common product is formed in these two reactions. This is confirmed by examination of the kinetic and chemical outcome of these reactions.

Photolysis of azirine **3** in acetonitrile solution in the absence of a trapping agent results in the slow formation of a deep red, dimeric product.<sup>55</sup> However, when dimethylmaleic anhydride (**4**) is included in the reaction solution, the dimer is not formed, and the azirine is converted to adduct **5**, which is the product anticipated to result from dipolar addition of acetonitrile ylide **6** to anhydride **4**<sup>48</sup> (Scheme III).

Analysis of the rate of reaction of the putative ylide generated from irradiation of azirine **3** with anhydride **4** is readily accomplished by monitoring the absorbance at 400 nm following laser pulse irradiation of the azirine. Kinetic analysis reveals a pseudo-first-order reaction with a bimolecular rate constant of  $5.3 \pm 0.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . This finding implicates the detected intermediate as the source of adduct **5** and supports its identification as ylide **6**.

Irradiation of DAF in an acetonitrile solution containing anhydride **4** gives both cyclopropane **7**, from reaction of the carbene (see below), and adduct **5** (Scheme III). Spectroscopic analysis following nanosecond laser photolysis reveals that the transient absorbing at 470 nm reacts with anhydride **4** in a pseudo-first-order process with a bimolecular rate constant of  $4.7 \pm 0.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . At low anhydride concentrations, some of this suspected carbene proceeds to form the transient product absorbing at 400 nm (eq 2) in competition with cyclopropanation of **4**. The second transient product, in turn, reacts with anhydride **4**, and the bimolecular rate constant for this reaction is the same as that obtained for reaction of the ylide formed directly from photolysis of azirine **3**. Analogous results are obtained when diethyl fumarate or diethyl ketomaleate are used to trap the ylide. These rate constants, and those for reaction of the ylide with other electron-deficient olefins, are summarized in Table I.

Confirmation that the detected transient products eventually give the isolated adducts comes from analysis of the relative yields of **5** and **7**. Photolysis of DAF in acetonitrile containing  $9.5 \times 10^{-2} \text{ M}$  **4** is predicted to give a ratio of yields of **7** to **5** + **3** (Scheme III) of 1.10, and experimentally the ratio obtained is  $1.11 \pm 0.1$ .

Individually, and in total, these findings demonstrate that the transient product absorbing at 400 nm formed from photolysis of DAF in acetonitrile is ylide **6** and not <sup>3</sup>Fl as we previously

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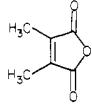
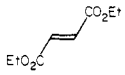
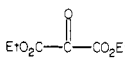

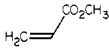

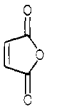
(52) Kende, A. S.; Hebeisen, P.; Sanfilippo, P. J.; Toder, B. H. *J. Am. Chem. Soc.* **1982**, *104*, 4244. Magee, W. L.; Shechter, H. *Tetrahedron Lett.* **1979**, 4697.

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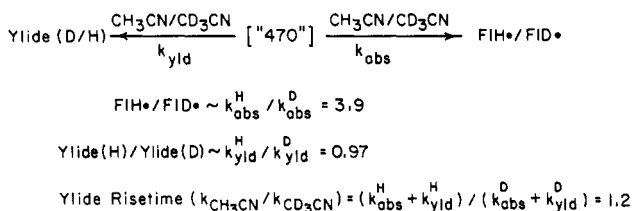
(54) A Lambda Physik Excimer Laser was used as the excitation source in this experiment.

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**Table I.** Reaction of Ylide 6 with Electron-Poor Olefins in Acetonitrile Solution

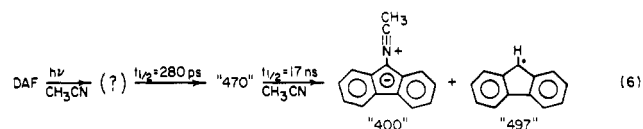
olefin	$k_T, M^{-1} s^{-1}$	
	DAF <sup>a</sup>	azirine 3 <sup>b</sup>
	$6.2 \times 10^5$	$5.3 \times 10^5$
	$9.1 \times 10^7$	$1.0 \times 10^8$
	$6.3 \times 10^8$	$4.5 \times 10^8$
	$4.7 \times 10^7$	c
	$2.0 \times 10^6$	c
	$7.1 \times 10^5$	c
	$9.8 \times 10^8$	c

<sup>a</sup> Ylide generated from photolysis of DAF and subsequent reaction of fluorenylidene with  $CH_3CN$ . Estimated error is  $\pm 10\%$  of the reported value. <sup>b</sup> Ylide generated directly from photolysis of azirine 3 in  $CH_3CN$ . Estimated error is  $\pm 10\%$  of the reported value. <sup>c</sup> Not determined.

**Scheme IV**

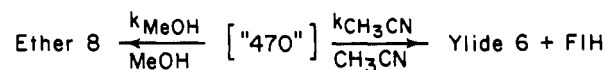
concluded. This has been suggested before<sup>2a,c</sup> and is consistent with the data of Griller and co-workers, who have reached a similar conclusion.<sup>42a</sup>

The consequences of substituting acetonitrile- $d_3$  for acetonitrile as solvent in the photolysis of DAF are particularly informative, especially when compared to a similar change in cyclohexane. Equation 6 indicates that the transient product responsible for



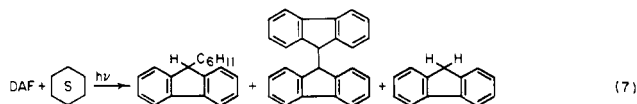
the 470-nm absorption band apparently undergoes two parallel reactions with acetonitrile. One is hydrogen atom abstraction to give  $FIH\cdot$ , and the second is an electrophilic reaction to give ylide 6. These reactions should respond differently to the solvent isotope change. Hydrogen abstraction is expected to exhibit a primary isotope effect, while ylide formation should be rather insensitive to this change.

The relative yields of ylide 6 and  $FIH\cdot$  in acetonitrile and acetonitrile- $d_3$  are obtained by measuring the absorbance change at 400 and 497 nm 150 ns after laser excitation, a time when formation of these products is complete, but before they have undergone any significant reaction. The product isotope effect obtained for radical formation ( $FIH\cdot/FID\cdot$ ) is  $3.9 \pm 0.5$  and for ylide generation is  $0.97 \pm 0.03$ . However, the kinetic isotope effect for formation of ylide ( $k_{CH_3CN}/k_{CD_3CN}$ ) obtained by measuring the rise time of the absorbance at 400 nm in the two solvents is  $1.2 \pm 0.03$ .

**Scheme V**

These results appear to show that a single intermediate (the transient product absorbing at 470 nm) is responsible for the triplet-carbene-like hydrogen atom abstraction and the singlet-carbene-like electrophilic addition to give ylide (Scheme IV). This dual character of fluorenylidene was observed earlier by Scaiano and co-workers<sup>42b</sup> but, following our lead, was misassigned to the singlet state.

**B. Photolysis in Cyclohexane.** Photolysis of DAF in cyclohexane solution gives the mixture of hydrocarbon products<sup>56</sup> shown in eq 7. These products may be formed either by hydrogen atom

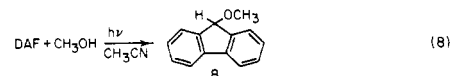


abstraction followed by radical disproportionation and combination reactions or by a combination of this abstraction-recombination sequence with direct insertion. The spectroscopic detection of  $FIH\cdot$  ensures that some abstraction has occurred. This is consistent with the isotope trace study of Baldwin and Andrist<sup>15</sup> in cyclohexane. However, it is still possible that direct insertion of the carbene, a typical singlet carbene process,<sup>1</sup> is proceeding simultaneously but is undetected. To examine this possibility, we undertook the comparison of cyclohexane and cyclohexane- $d_{12}$  as solvents in this reaction.

The search for direct insertion into the carbon-hydrogen bonds of cyclohexane by fluorenylidene is based in part on the assumption that insertion will show a different isotope effect (presumably smaller) than abstraction. Phenylcarbene is reported<sup>29</sup> to discriminate competitively between the carbon-hydrogen and carbon-deuterium bonds of cyclohexane with an isotope effect of 2.1. Thus, if insertion is competing with abstraction, we anticipate that fewer 9-fluorenyl radicals will be formed in the deuterated solvent.

The relative yields of  $FIH\cdot$  and  $FID\cdot$  in cyclohexane and cyclohexane- $d_{12}$  were determined by measuring the absorbance change at 497 nm 100 ns after laser irradiation of DAF. The observed isotope effect is  $1.08 \pm 0.09$ . However, the rate of formation of the fluorenyl radical is different in these two solvents and shows an isotope effect of about 2. These results show that within experimental error there is no reaction with a significant rate and a different isotope effect, competing with hydrogen abstraction by the carbene in cyclohexane solution.

**C. Reaction with Alcohols.** The formation of an ether from the reaction of an alcohol with a carbene has generally been identified with the singlet state.<sup>6-8,10-12</sup> Photolysis of DAF in acetonitrile containing methanol gives methyl fluorenyl ether 8 in isolated yield up to 95% (eq 8). This reaction was examined spectroscopically by using the nanosecond laser equipment.



As the methanol concentration in an acetonitrile solution of DAF is increased, the apparent rate of consumption of the transient product absorbing at 470 nm is increased, and concomitantly, the rate of appearance of nitrile ylide 6 also increases (rate constant  $k_{obsd}$ ). The relative yield of ylide 6 ( $\phi_{yld}$ ), however, decreases monotonically as the concentration of methanol in the solution increases, and, at 0.2 M, ylide becomes undetectable. These findings show that the carbene absorbing at 470 nm, and identified by low temperature spectroscopy as <sup>3</sup>Fl, is apparently reacting with methanol to give ether 8 (Scheme V).

The apparent rate constant for reaction of fluorenylidene with methanol ( $k_{MeOH}$ ) was obtained by two independent techniques.

(56) Kirmse, W.; Horner, L.; Hoffmann, H. *Liebigs Ann. Chem.* **1958**, 614, 19.

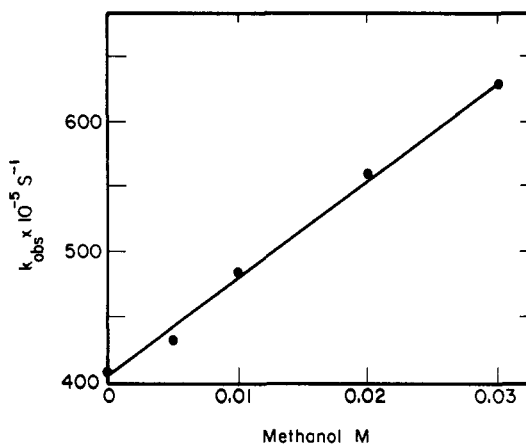


Figure 7. Kinetic analysis of the rate constant for reaction of methanol with equilibrated fluorenylidene in acetonitrile at room temperature.  $k_{obs}$  is the observed rate constant for the growth of ylide 6.

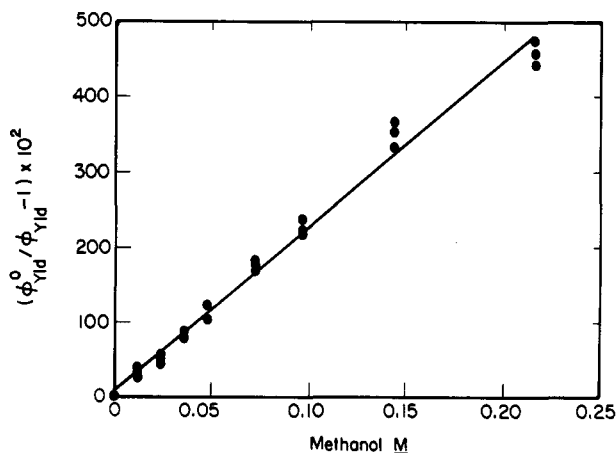


Figure 8. Stern-Volmer analysis of the rate constant for reaction of methanol with equilibrated fluorenylidene in acetonitrile at room temperature.

First, we measured  $k_{obs}$  as we increased the methanol concentration and analyzed the results according to eq 9 (Figure 7). This

$$k_{obs} = k_{CH_3CN} [CH_3CN] + k_{MeOH} [MeOH] \quad (9)$$

$$\phi_{Yld} = \frac{k_{CH_3CN} [CH_3CN]}{k_{CH_3CN} [CH_3CN] + k_{MeOH} [MeOH]} \quad (10)$$

procedure gives  $k_{MeOH} = 8.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . Second, we obtained the relative yields of ylide 6 by monitoring the absorbance change at 400 nm as a function of methanol concentration and analyzed the results by the Stern-Volmer technique (eq 11), where  $\phi^0_{Yld}$

$$\left( \frac{\phi^0_{Yld}}{\phi_{Yld}} - 1 \right) = \frac{k_{MeOH}}{k_{CH_3CN} [CH_3CN]} [MeOH] \quad (11)$$

is the yield of ylide with no methanol present (Figure 8). This procedure gives  $k_{MeOH} = 8.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . Thus, both procedures give an apparent rate constant for a singlet-carbene reaction, originating from an apparent triplet carbene, about 20 times slower than the diffusion-controlled limit. In this case we do not detect any evidence of the concentration dependence of the rate constant for reaction with alcohols that has been seen with phenylchlorocarbene.<sup>12</sup> This may indicate that the rate of reaction of fluorenylidene with monomeric methanol is the same as that for the associated forms. The rate constants for reaction of fluorenylidene with several alcohols are summarized in Table II.

To investigate the dilemma posed by observation of a singlet carbene reaction from an apparent triplet carbene, we examined the triplet sensitization of DAF in acetonitrile containing methanol.

Table II. Reaction of Equilibrated Fluorenylidene with Alcohols

alcohol	solvent	$10^{-8}k_r, \text{M}^{-1} \text{s}^{-1} \text{ }^a$
CH <sub>3</sub> OH	CH <sub>3</sub> CN	8.6
CH <sub>3</sub> OH	C <sub>6</sub> F <sub>6</sub>	1.2
C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> CN	7.3
C <sub>2</sub> H <sub>5</sub> OH	C <sub>6</sub> F <sub>6</sub>	2.4
(CH <sub>3</sub> ) <sub>2</sub> CHOH	CH <sub>3</sub> CN	5.2
(CH <sub>3</sub> ) <sub>2</sub> CHOH	C <sub>6</sub> F <sub>6</sub>	0.98

<sup>a</sup> Observed rate constant for reaction with equilibrated fluorenylidene. The error is estimated to be  $\pm 10\%$  of the reported value.

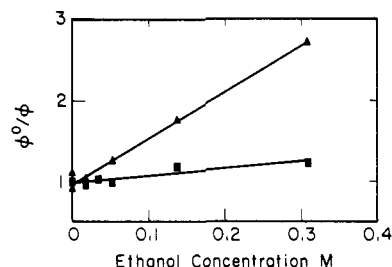


Figure 9. Stern-Volmer analysis of the formation of FIH· (triangles) and initially formed fluorenylidene (squares) as the concentration of ethanol is increased in spiropentane at room temperature.

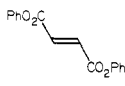
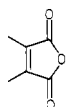
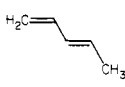












Triplet thioxanthone is quenched by DAF in acetonitrile, presumably forming first triplet DAF, which subsequently loses N<sub>2</sub> to form <sup>3</sup>Fl. Thus, sensitization should bypass <sup>1</sup>Fl, which is formed first in the direct photolysis of DAF. Irradiation of an acetonitrile solution of DAF ( $9.2 \times 10^{-4} \text{ M}$ ) containing thioxanthone ( $8 \times 10^{-4} \text{ M}$ ) and methanol (0.5 M) at 380 nm, where thioxanthone absorbs essentially all of the light, gives ether 8 in 92% isolated yield. A control experiment, in which 2,5-dimethyl-2,4-hexadiene (0.05 M) was included in the above reaction mixture as a quencher of thioxanthone triplet, gives only a 2% yield of ether 8 after identical irradiation. These results indicate that under these conditions, conversion of <sup>3</sup>Fl to <sup>1</sup>Fl, and subsequent reaction of the latter with methanol, is an important reaction channel for fluorenylidene, just as it appears to be for diphenylmethylene.<sup>8,18</sup> The kinetic results show, however, that equilibrated fluorenylidene is ca. 130 times more reactive toward methanol than is equilibrated diphenylmethylene. This can be a consequence of the higher inherent reactivity of <sup>1</sup>Fl toward methanol, or, as we suggest below a higher relative concentration of <sup>1</sup>Fl in equilibrated fluorenylidene.<sup>57</sup>

The investigation of the reaction of fluorenylidene with alcohols in hydrocarbon solution gives analogous results. Nanosecond laser photolysis reveals that when low concentrations of ethyl alcohol (methanol is insoluble) are added to DAF in spiropentane solution both FIH·, absorbing at 497 nm, and the triplet carbene, absorbing at 470 nm, can still be detected. Addition of the alcohol causes the rate of decay of <sup>3</sup>Fl and the rate of growth of FIH· to increase but alters only slightly the amount of <sup>3</sup>Fl initially formed, as indicated by the absorbance change at 470 nm extrapolated to  $t = 0$ . However, the amount of FIH· formed eventually, as measured by the absorbance change at 497 nm 120 ns after pulse irradiation, is reduced significantly by the addition of the ethyl alcohol (Figure 9). These results indicate that <sup>3</sup>Fl, responsible for hydrogen abstraction, and <sup>1</sup>Fl, responsible for ether formation, are in equilibrium in the hydrocarbon solution under these conditions. Moreover, attainment of equilibrium is somewhat faster than the reaction of <sup>1</sup>Fl under these conditions.

Finally, the apparent rate constant for reaction of equilibrated fluorenylidene with alcohols in hexafluorobenzene was determined. The decay rate of fluorenylidene, obtained by monitoring the time dependence of the absorbance at 470 nm, was evaluated at in-

(57) The rate constants we report in the text and tables are those observed experimentally for a particular reactant with equilibrated fluorenylidene (both <sup>1</sup>Fl and <sup>3</sup>Fl) in a particular solvent. To obtain the actual rate constant for reaction, the equilibrium constant in that solvent must be known; see Discussion section.

Table III. Reaction of Equilibrated Fluorenylidene with Olefins

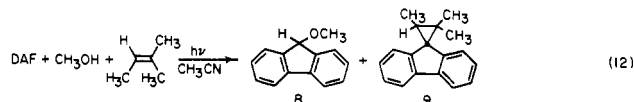
olefin	$10^{-8}k_{r_1}$ $M^{-1} s^{-1}^a$	olefin	$10^{-8}k_{r_1}$ $M^{-1} s^{-1}^a$
	15		4.7
	10		3.5
	9.4		3.2
	4.6		
(C <sub>6</sub> F <sub>6</sub> solvent)			
	7.8		1.9
	6.7		2.2
	1.3	(Freon 113 solvent)	
			0.28
	1.4		0.17

<sup>a</sup> Observed rate constant for reaction with equilibrated fluorenylidene in acetonitrile solution unless otherwise noted. The uncertainty in the rate constants is estimated to be ca.  $\pm 10\%$  of the reported value.

creasing methanol concentrations. Analysis of these data, through appropriate adaptation of eq 9, gives the rate constants shown in Table II. It should be noted that the apparent reactivities of fluorenylidene toward these alcohols in hexafluorobenzene is ca. 5 times less than in acetonitrile.

**D. Reaction with Olefins.** One of the often noted endearing properties of fluorenylidene is the high yield of cyclopropanes that result from its reaction with nearly all olefins.<sup>19,27,58</sup> We have examined this cyclopropanation reaction in some detail.

Photolysis of DAF in acetonitrile containing 2-methyl-2-butene, for example, gives the appropriate cyclopropane (**9**) in high yield (eq 12). Using the spectroscopic techniques described above for









methanol, we observe that addition of the olefin increases the rate of reaction of the carbene absorbing at 470 nm and concomitantly decreases the yield of ylide **6**. Using the Stern–Volmer approach outlined in eq 11, we obtain a rate constant for reaction of equilibrated fluorenylidene with 2-methyl-2-butene of  $3.5 \times 10^8 M^{-1} s^{-1}$ . The rate constants for reaction of other olefins with fluorenylidene are summarized in Table III.

Final verification that the transient product we detect spectroscopically at 470 nm is fluorenylidene and that the rate constants we measure correspond actually to formation of the products eventually isolated comes from a series of quantitative competition experiments. Photolysis of an acetonitrile solution of DAF containing both an olefin and methanol gives both ether **8** and cyclopropane (eq 12). The concentrations of alcohol and olefin are sufficiently high so that formation of ylide **6** does not occur. Under these conditions the ratio of the yield of cyclopropane ( $\phi_{\text{cyp}}$ ) to the yield of ether ( $\phi_{\text{ether}}$ ) is given by eq 13, where  $k_{\text{olefin}}$  is the

$$\frac{\phi_{\text{cyp}}}{\phi_{\text{ether}}} = \frac{k_{\text{olefin}}[\text{olefin}]}{k_{\text{MeOH}}[\text{MeOH}]} \quad (13)$$



(58) Shimizu, N.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1972**, 389. Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1974**, *96*, 6451.

Table IV. Quantitative Competition of Fluorenylidene between Methanol and Olefins

olefin	concn, M	MeOH, M	$\phi_{\text{cy}}/\phi_{\text{ether}}$	cyclopropane <sup>a</sup> / ether
	1.15	0.94	1.45	1.40
	2.54	0.33	1.65	1.79
	2.38	0.33	2.28	2.43
	2.38	0.26	1.31	1.27
	2.21	0.82	0.38	0.39
	2.70	0.30	1.44	1.39 <sup>b</sup>
	2.13	0.92	0.41	0.36
	6.48	0.20	1.5	1.2 <sup>c</sup>

<sup>a</sup> Product ratio determined by gas chromatography or by integration of the <sup>1</sup>H NMR spectrum. <sup>b</sup> There is significant CH insertion with this olefin (18%), and  $\phi_{\text{cyp}}$  is taken as the sum of insertion and cyclopropane products. <sup>c</sup> In this case the cyclopropane product yield is taken to include that of rearranged dichloride **11** also.

Table V. Stereochemical Consequence of Olefin Dilution

olefin, M	added reagent	additive concn, M	cis	
			cis + trans <sup>a</sup>	
	9.25 (neat)			0.68
	8.18	CH <sub>3</sub> CN	2.22	0.70
	7.02	CH <sub>3</sub> CN	4.63	0.69
	4.68	CH <sub>3</sub> CN	9.45	0.69
	3.51	CH <sub>3</sub> CN	11.9	0.68
	2.34	CH <sub>3</sub> CN	14.3	0.65
	2.38	MeOH <sup>b</sup>	0.82	0.62
	1.94	CH <sub>3</sub> CN	14.4	0.46
	2.54	MeOH <sup>b</sup>	0.33	0.46
	0.2	MeOH <sup>b</sup>	0.80	0.45
	2.24	Freon 113	6.93	0.41

<sup>a</sup> Yield of the *cis*-cyclopropane in the mixture of cyclopropanes. <sup>b</sup> The remainder of the solution is acetonitrile.

measured bimolecular rate constant for reaction of the olefin with the transient product absorbing at 470 nm. The results of these experiments are displayed in Table IV. Within experimental error, in every case examined, eq 13 accurately predicts the actual ratio of products obtained.


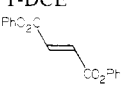
The stereochemical outcome of olefin cyclopropanation by fluorenylidene is intriguing. Irradiation of DAF in neat *trans*-olefin gives *trans*-cyclopropane and little, if any, of the *cis* isomer. Alternatively, irradiation in neat *cis*-olefin gives a mixture of *cis*- and *trans*-cyclopropanes. Control experiments show that the formation of the *trans*-cyclopropane from the *cis*-olefin is not a consequence of prior olefin isomerization or isomerization of the cyclopropane subsequent to its formation.

In contrast to the behavior reported by Jones and Rettig<sup>26</sup> for dilution of neat olefin with hexafluorobenzene, we find that dilution with acetonitrile, methanol, or Freon 113 has no effect on the stereochemical outcome of the cyclopropanation of *cis*-2-pentene or *cis*- $\beta$ -methylstyrene by fluorenylidene (Table V). These results are consistent with attainment and maintenance of equilibrium between <sup>1</sup>Fl and <sup>3</sup>Fl in the presence of those olefins and other reagents. In this situation, it is not possible to assign a particular stereochemical outcome to a specific electronic state of the carbene.

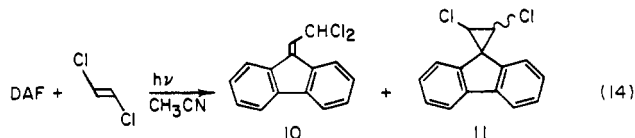
The reactions of *cis*- and *trans*-1,2-dichloroethylene (C-DCE and T-DCE) with fluorenylidene also point to competitive reformation of <sup>1</sup>Fl and <sup>3</sup>Fl. Photolysis of DAF in acetonitrile solution containing 6.48 M T-DCE gives rearranged dichloride **10** and *cis*-



**Table VI.** Effect of Added Reagents on the Reaction of Fluorenylidene with *cis*- and *trans*-Dichloroethylene in Acetonitrile Solution

reagents	concn, M	11	
		10 + 11	trans + cis
T-DCE	6.48	0.75	0.85
C-DCE	6.48	0.80	0.15
T-DCE	6.48	0.78	0.78
CH <sub>3</sub> OH	0.2		
T-DCE	6.48	0.78	0.81
	0.3		
T-DCE	6.48	0.78	0.83
	$3.6 \times 10^{-3}$		

and *trans*-cyclopropanes **11**, along with fluorenone and a small amount of 9-chlorofluorene<sup>59</sup> (eq 14).



The rate constants for reaction of C-DCE and T-DCE with fluorenylidene are reported in Table III. We examined the effect of various competitive trapping reagents on the ratio of rearrangement (a presumed triplet carbene reaction) to cyclopropanation (suggested to come from both the singlet and triplet carbene) and on the stereochemical outcome of the cyclopropanation reaction. The results are presented in Table VI. It appears that the added reagents do not change the measured product ratios. Addition of methanol, which presumably reacts with <sup>1</sup>F1, styrene, which may react with both <sup>1</sup>F1 and <sup>3</sup>F1, and diphenyl fumarate, which reacts rapidly with ylide **6**, all leave the ratio of **10** to **11** unchanged and similarly do not change the stereochemical outcome of cyclopropanation. These findings also are consistent with maintenance of equilibrium between <sup>1</sup>F1 and <sup>3</sup>F1 under these reaction conditions.

### Discussion

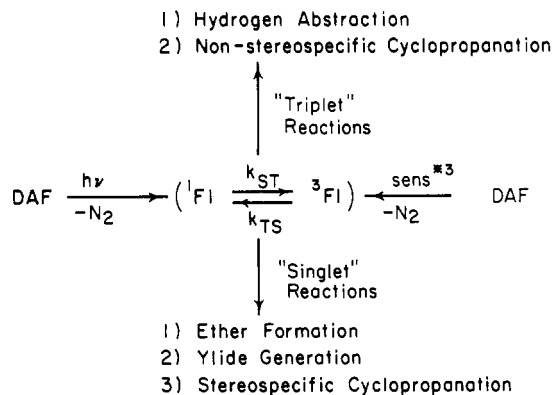
The results described above and revised assignments point to a description of the properties of fluorenylidene consistent with those of the other arylcarbenes that have been investigated (Scheme VI). The central feature of this scheme is rapid interconversion between <sup>1</sup>F1 and <sup>3</sup>F1 compared to many of the bimolecular reactions of these species. The spectroscopic and chemical studies we have carried out support this conclusion and provide some information on the rates of intersystem crossing from <sup>3</sup>F1 to <sup>1</sup>F1 (*k*<sub>TS</sub>) and vice versa (*k*<sub>ST</sub>). In turn, these rates provide an estimate of the energy difference between the lowest states of fluorenylidene.

The low-temperature spectroscopy clearly indicates the assignment of the 470-nm absorption band to <sup>3</sup>F1. All of the laser kinetic and spectroscopic results support that assignment and additionally implicate <sup>1</sup>F1 as a spectroscopically undetected companion to the triplet at room temperature.<sup>60</sup> The picosecond laser experiments reveal that <sup>3</sup>F1 is not formed "instantaneously" but grows with a rate somewhat dependent on solvent from an unseen precursor. There are two reasonable structures for the unseen precursor, <sup>1</sup>F1 and triplet DAF (the question marks in eq 2, 4, and 6).

(59) Funakubo, E.; Moritani, I.; Nagai, T.; Nishida, S.; Murahashi, S.-I. *Tetrahedron Lett.* **1963**, 1069. These authors claim that 9-chlorofluorene is the major product of the reaction of fluorenylidene with T-DCE. Our experience is that this product is a consequence of a ground-state reaction of DAF and HCl.

(60) The lowest energy optical absorption for the triplet is expected to be an allowed  $\pi\pi^*$  transition, whereas the  $\sigma^2$  singlet should exhibit a much weaker  $n\pi^*$  band.

### Scheme VI



It is not possible to be unequivocal in the assignment of the precursor of <sup>3</sup>F1 with the data in hand. However, as noted by Roth,<sup>14</sup> in cases where chemical reactions of singlet carbenes are clearly delineated, loss of nitrogen by excited singlet diazo compound to generate singlet carbene is the exclusive result. Intersystem crossing to triplet diazo compound does not compete with this reaction. Similarly, Eisenthal and co-workers<sup>61</sup> conclude, based on a study of the fluorescence of triplet diphenylmethylenes on a picosecond time scale, that the dominant pathway for the production of this carbene is by intersystem crossing of the nearby singlet state, and not from excited diazo compound. Finally, a study of Griffin and co-workers<sup>62</sup> of the photochemical generation of phenylcarbene from diverse sources shows that this carbene's properties are independent of its source, thus eliminating a chemical role for excited diazo compound. For these reasons, we choose to attribute the observed rise time of <sup>3</sup>F1 following picosecond excitation of DAF to its attainment of equilibrium with the first-formed <sup>1</sup>F1.

The rate of re-formation of <sup>3</sup>F1 from <sup>1</sup>F1 can be estimated from the reactivity data reported above. There has been general agreement that formation of ethers from alcohols is a singlet carbene reaction. Moreover, the rate of reaction of singlet diphenylmethylenes with methanol was first assumed<sup>18</sup> and then shown experimentally<sup>19</sup> to occur at approximately a diffusion-controlled rate. If we assume that the reaction of <sup>1</sup>F1 with methanol in acetonitrile occurs with a rate no faster than that of diffusion (*k*<sub>diff</sub> =  $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ), then we can estimate an upper limit for the equilibrium constant ( $K_{\text{eq}} = k_{\text{ST}}/k_{\text{TS}} = [^3\text{F1}]/[^1\text{F1}]$ ) for the fluorenylidene spin states in acetonitrile from eq 15, where

$$K_{\text{eq}} \leq k_{\text{diff}}/k_{\text{MeOH}} \quad (15)$$

*k*<sub>MeOH</sub> is the rate constant we obtained for reaction of equilibrated fluorenylidene with methanol. This procedure gives  $K_{\text{eq}} \leq 22$ , which indicates that there is ca. 5%, or more, <sup>1</sup>F1 present at equilibrium. From the rise time of <sup>3</sup>F1 measured in acetonitrile by picosecond spectroscopy, we obtain  $k_{\text{ST}} = 2.5 \times 10^9 \text{ s}^{-1}$ , and from this value and  $K_{\text{eq}}$  division gives  $k_{\text{TS}} \geq 1.1 \times 10^8 \text{ s}^{-1}$ . From these findings and the assumption that ethers are formed only from singlet carbenes, the enthalpy difference between <sup>1</sup>F1 and <sup>3</sup>F1 ( $\Delta E_{\text{ST}}$ ) is calculated to be less than or equal to 1.1 kcal/mol.<sup>63</sup> This small an energy gap indicates considerable mixing between pure spin states and may give the "triplet" significant "singlet" character (and vice versa). In this circumstance the assignment of unique chemical properties to specific carbene spin states may be inappropriate.

The conclusion that <sup>1</sup>F1 and <sup>3</sup>F1 can equilibrate is consistent with all of the results we have obtained, but, at first glance, appears to be at odds with the experiments of Jones and Rettig<sup>26,36</sup> that have previously been used to support the notion of unidirectional

(61) Dupuy, C.; Korenowski, G. M.; McAuliffe, M.; Hetherington, W. M., III; Eisenthal, K. B. *Chem. Phys. Lett.* **1981**, *77*, 272.

(62) Dietrich, H.; Griffin, G. W.; Petterson, R. C. *Tetrahedron Lett.* **1968**, 153.

(63) This value assumes that  $\Delta S$  for <sup>1</sup>F1 and <sup>3</sup>F1 is the same except for the statistical factor.

(64) Bedsole, A. D.; Taylor, Z. L., Jr. *J. Ala. Acad. Sci.* **1968**, *39*, 270.

intersystem crossing. In one of these experiments,<sup>36</sup> it was observed that addition of high concentrations of butadiene to *cis*-2-butene solutions of DAF increased the stereospecificity of the olefin cyclopropanation. It was argued that <sup>1</sup>Fl, in contrast to <sup>3</sup>Fl, reacts stereospecifically, and that the diene reacts preferentially with <sup>3</sup>Fl. We have not measured the rate of reaction of fluorenylidene with butadiene because, being a gas, its concentration is difficult to control. However, we have measured the rate constant for reaction of fluorenylidene with *trans*-1,3-pentadiene (Table III) and find it to be  $1.03 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in acetonitrile. At the concentrations employed by Jones and Rettig, the rate of reaction of <sup>3</sup>Fl with the diene is likely to be no smaller than  $1 \times 10^9 \text{ s}^{-1}$ . When this value is compared with  $k_{\text{TS}}$  calculated above, it is clear that under these conditions reversion to <sup>1</sup>Fl does not compete with the other reactions of <sup>3</sup>Fl, and equilibrium is not maintained.

The second experiment<sup>26</sup> showed that dilution of a *cis*-2-butene solution of DAF with hexafluorobenzene decreases the stereospecificity of olefin cyclopropanation. It was suggested that the hexafluorobenzene is acting as an inert diluent providing a non-reactive collision partner and allowing intersystem crossing to <sup>3</sup>Fl to occur. Our spectroscopic and product studies reveal that hexafluorobenzene is not inert, nor does it increase significantly the rate of <sup>3</sup>Fl appearance. Instead, the results of the kinetic and product studies indicate that equilibrium is achieved and maintained throughout the concentration range studied. We suspect that the true effect of hexafluorobenzene in these dilution experiments is to increase slightly the energy difference between <sup>1</sup>Fl and <sup>3</sup>Fl and thereby increases the fraction of reaction occurring from <sup>3</sup>Fl. Similar suggestions of a solvent effect on the equilibrium constant connecting singlet and triplet diphenylmethylene have been made.<sup>19,20</sup> Also, a solvent-dependent equilibrium constant accommodates the effect observed by Shimizu and Nishida<sup>58</sup> when benzene is used to dilute the reaction of fluorenylidene with 1,1-dicyclopropylethylene.

Some evidence for this suggested solvent-dependent change in equilibrium constant comes from examination of the observed rates of reaction of methanol with equilibrated fluorenylidene in acetonitrile and hexafluorobenzene solutions. The data in Table II show a ca. 7-fold decrease in the rate constant for reaction accompanying this solvent change. If we continue to assume that the reaction of methanol with <sup>1</sup>Fl is diffusion limited in both solvents, then this change can be interpreted to reflect the change in the equilibrium constant. Calculation of the equilibrium constant in hexafluorobenzene according to eq 15 ( $k_{\text{diff}} = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>64</sup> gives  $K_{\text{eq}} \leq 68$ . Thus, this analysis indicates that there is considerably less <sup>1</sup>Fl in the equilibrium mixture in the benzene than in acetonitrile or neat olefin (which give the same stereochemical outcome, Table IV). Of course, relatively less <sup>1</sup>Fl implies decreased stereospecificity in the cyclopropanation reaction.

Finally, the results described above provide additional insight into the often noted chemical differences between fluorenylidene and diphenylmethylene. One clear difference is the magnitude of the energy gap between the corresponding singlet and triplet states. This change of ca. 3 kcal/mol accounts for a ca. 150-fold difference in the equilibrium population of the respective singlet carbenes and thereby explains the enhanced reactivity of equilibrated fluorenylidene with alcohols, for example.

The smaller energy gap of the fluorenylidene states compared with those of diphenylmethylene can in principle be brought about by either lowering the singlet of the former with respect to its triplet or by raising the triplet with respect to its singlet. The second explanation is more consistent with the results. We note that fluorenylidene reacts with 1,3-pentadiene ca. 3000 times more rapidly than diphenylmethylene reacts with 2-methyl-1,3-butadiene.<sup>19</sup> This increased reactivity can be associated with a higher energy, thus more reactive, triplet carbene. In this regard, the increased energy and reactivity of <sup>3</sup>Fl may be traced to the enforced contraction of the carbene carbon bond angle to 108° from 136° in triplet methylene.<sup>65</sup> We are presently conducting ex-

periments designed to test this hypothesis.

## Experimental Section

**General.** Proton magnetic resonance (<sup>1</sup>H NMR) spectra were recorded on Varian Associates EM-390 (90 MHz) or HR220 (220 MHz), operated in either CW or FT mode) spectrometers or on the NSF Midwest Regional NMR Center's Nicolet NT360 (360 MHz, operated in FT mode with deuterium lock) spectrometer in deuteriochloroform (unless otherwise noted) with tetramethylsilane as an internal standard. Carbon magnetic resonance spectra (<sup>13</sup>C NMR) were recorded on a JEOL FX-60 (60 MHz) spectrometer. Mass spectra (MS) were obtained with Varian MAT CH-5 and 731 mass spectrometers. Infrared absorption (IR) spectra were recorded on a Perkin-Elmer Model 237B grating spectrophotometer and a Nicolet 7199 FT-IR instrument. Steady-state ultraviolet-visible (UV-vis) absorption spectra were recorded with a Perkin-Elmer Model 552 or a Cary 14 spectrophotometer. Electron paramagnetic resonance (EPR) spectra were recorded on a Varian Associates E-4 (X-Band) spectrometer. EPR spectra at 10 K were obtained with the help of M. Hendrich and Dr. P. DeBrunner of the University of Illinois Physics Department of a Bruker instrument. Elemental analyses were performed by the Analysis Laboratory, University of Illinois. Melting points were determined in sealed capillary tubes employing a Büchi Schmelzpunktbestimmungsapparat and are uncorrected. High-performance liquid chromatography (HPLC) was performed with a Perkin-Elmer Series 2 liquid chromatograph equipped with variable wavelength detector using 10- $\mu$  silica columns (0.26  $\times$  25 cm analytical or 5  $\times$  25 cm preparative) with 0.5% 2-propanol in hexane as elutant. Analytical reverse-phase HPLC was performed by using a C8 packing (0.46  $\times$  25 cm) with 40% water in acetonitrile as the elutant at 1.5 mL/min. Analytical gas chromatography (GC) was performed with a Varian Aerograph Model 2700 or a Hewlett-Packard 5790A gas chromatograph equipped with linear-temperature programmer and a flame ionization detector; 1.5-m silanized glass columns containing SE-30 or OV-101 on dichlorodimethylsilane-treated Chromasorb W were used with helium as the carrier gas at 20 psi.

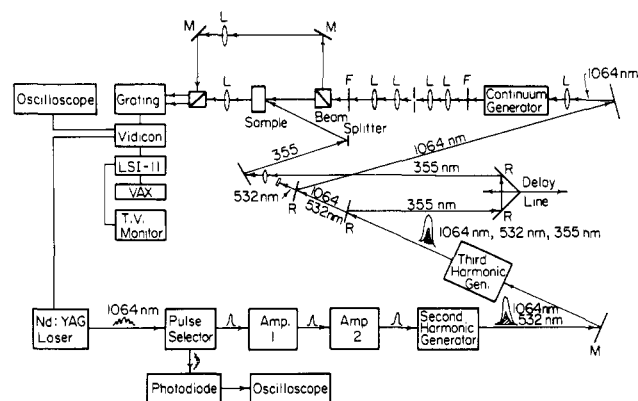
**Materials.** Acetonitrile (Aldrich Gold Label) for laser spectroscopy was refluxed for 4 h over CaH and distilled under nitrogen by using a 3-m vacuum-jacketed column packed with glass helices with a high reflux ratio. Freon 113 (Matheson) was shaken in turn with sulfuric acid and aqueous sodium carbonate, then dried with magnesium sulfate, and distilled from phosphorus pentoxide. Methylcyclohexane (Aldrich 99%) was shaken twice with a mixture of concentrated sulfuric acid and nitric acids, washed thoroughly with water, and dried over and distilled from calcium chloride. 2-Methyltetrahydrofuran (Aldrich) was passed through a column of neutral alumina (Woelm, activity grade I) and distilled from calcium hydride. Spiropentane was prepared from pentaerythritol tetrabromide by the method of Applequist et al.<sup>46</sup> The crude spiro-pentane was titrated with bromine in ethylene dibromide to remove olefinic impurities and distilled under nitrogen by using a 1-m vacuum-jacketed column packed with glass helices (bp 36–38 °C). *cis*- and *trans*-2-pentene, *cis*- and *trans*-propenylbenzene, *cis*- and *trans*-4-methyl-2-pentene, and diethyl maleate were obtained from Wiley Organics and were used without prior purification. *trans*-1,2-Dichloroethylene (Aldrich) was distilled prior to use (1-m vacuum-jacketed column packed with glass helices) and stored over anhydrous sodium carbonate. *cis*-1,2-Dichloroethylene was prepared from the *trans* isomer by Gaspar's<sup>20</sup> method and also stored over anhydrous sodium carbonate. The isomeric purity of this olefin was determined by 220-MHz <sup>1</sup>H NMR. Diazofluorene was prepared by the oxidation of the hydrazone using HgO, mp 96–98 °C (lit.<sup>66</sup> 94–95 °C). Diphenyl fumarate was prepared by treatment of fumaryl chloride (Aldrich) with phenol (Allied) in refluxing benzene and purified by sublimation. 9-Hydroxyfluorene was prepared by sodium borohydride reduction of 9-fluorenone in methanol and recrystallization from low-boiling petroleum ether. 9-Chlorofluorene was prepared by treatment of 9-hydroxyfluorene with thionyl chloride and recrystallization from methanol. Methyl fluorenyl ether **8** was prepared by the method of Kliegl.<sup>67</sup> Satisfactory elemental and spectral analyses were obtained for all compounds.

**Picosecond Spectroscopy.** In the picosecond absorption experiments discussed herein a Quantel YG40 Nd:YAG laser system with Kodak 9740 mode-locking dye was used. As illustrated in Figure 10, firing the laser flashlamps generates a train of 1064-nm pulses ca. 30 ps in duration and separated by ca. 7 ns, which are emitted through the laser output etalon. These pulses then pass through a pulse selector, which allows one pulse from the train to continue down the table and sends the remainder of the train into a photodiode whose output is monitored on a Tektronix 7834 storage oscilloscope, with 7B80 time base. The selected pulse is

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**Figure 10.** Schematic diagram of the picosecond spectrometer. The symbols are as follows: L = lens, M = mirror, R = dichroic reflector, F = filter.

then amplified twice, giving an infrared pulse of approximately 25 mJ in energy. This IR pulse is sent through a KD\*P type II second-harmonic crystal and then a KD\*P type II third-harmonic crystal. The third-harmonic beam, 355 nm, 3–5 mJ, is reflected into moveable mirrors along a delay line, and after appropriate filtering it reaches the sample. Residual IR light is focused into a 10-cm long cell of carbon tetrachloride, using a 50-cm focal length lens. After the cell any remaining IR is removed from the white light, and the beam is then collimated and focused onto a pinhole. The beam then is recollimated, focused, sent through an aperture, and split in two. One of the beams passes through the sample and the other is used as a reference. After the sample these beams are both sent into a two-dimensional optical multichannel analyzer consisting of an Instruments SA UFS-200 spectrograph and a Princeton Applied Research 1254 silicon-intensified target detector head. Output from this detector is then digitized and stored on a DEC LSI 11/03 computer, as discussed elsewhere.<sup>68</sup> The detector has been modified as suggested by Liesegang and Smith.<sup>69</sup>

Digitized data is monitored on a Matrox TV monitor board (MX-512). Acceptance of each laser shot is based upon the quality of the laser train (monitored on the oscilloscope) and by the smoothness and intensity of the reference white-light continuum beam. A typical spectrum is an average of ten laser shots in which the sample was excited and ten in which it was not, alternating excitation and no-excitation shots throughout the data run. Spectra are taken at various delays between the UV excitation pulse and the probing continuum pulse. These delays are varied by changing the position of the moveable UV mirrors. Spectra range from 440 to 525 nm, can be taken up to a maximum delay of 4 ns after excitation, and may be smoothed by Quartic Polynomial smoothing.<sup>70</sup>

**Low-Temperature UV-vis Spectra.** Low-temperature spectra at 77 K were obtained by using a three-window (Pyrex) optical Dewar filled with liquid nitrogen. The sample was dissolved in dry 2-methyltetrahydrofuran, placed in a long-necked Pyrex cuvette, closed with a septum, and cooled in the liquid nitrogen. After a base line had been recorded, the sample was irradiated for several minutes in the spectrophotometer with a Hanovia 450-W high-pressure mercury lamp. Subtraction of the base line provides the desired spectral data. Substitution of the liquid-nitrogen-filled optical Dewar with an Oxford-cryostat Dewar equipped with quartz outer windows and sapphire inner windows and a liquid-helium transfer line permitted spectra to be obtained at 10 K.

**Low-Temperature EPR Spectrum of Triplet Fluorenylidene.** A 0.018 M solution of diazofluorene in 2-methyltetrahydrofuran was placed in a quartz tube, nitrogen was blown over the solution, and then it was capped with a septum and with Parafilm. The sample was cooled to 10 K and irradiated with a Hanovia 450-W high-pressure mercury lamp in the EPR cavity. Three signals were observed at 990, 4560, and 5680 G. A fourth signal was inadvertently not scanned. After warming to 77 K and recooling, no signals could be observed.

**General Sample Preparation for Laser Spectroscopy.** A stock solution of DAF in a particular solvent was prepared so that a sample of the appropriate path length would absorb a significant portion of the laser light. Generally, these solutions were ca.  $1 \times 10^{-3}$  M for the nanosecond experiments (337-nm excitation) and  $5 \times 10^{-3}$  M for the picosecond experiments (355-nm excitation). These solutions were placed in a 10-

mm (nanosecond) or 2-mm (picosecond) path cell equipped with a stir bar and Teflon stopcock. Oxygen was removed by purging the solution with dry nitrogen for 4 min. The samples were stirred between shots and changed at frequent intervals (maximum of 15 pulses on the nanosecond laser, 30 pulses on the picosecond equipment). In no case was there observed any power dependence, or any dependence on the prior history of the sample.

**3-Methylspiro[2H-azirine-2,9'-[9H]fluorene] (3).** This compound was prepared by the methods of Smolinsky and Pryde,<sup>53</sup> except we were unable to obtain the intermediate, ethyl 2-fluorenylideneacrylate, as described. Rather we isolated ethyl 2-(9-hydroxy-9-fluorenyl)propionate, which could be dehydrated to the desired product by refluxing overnight in a benzene solution with a catalytic amount of *p*-toluenesulfonic acid employing a Dean-Stark trap to collect azeotroped water. Failure to dehydrate the hydroxy ester as described above resulted in quantitative formation of fluorenone in the subsequent saponification. Sublimation and recrystallization of the azirine from methanol gives white plates: mp 97–98 °C (lit.<sup>53</sup> 97–99 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.65 (s, 3 H, methyl), 6.90–7.80 (m, 8 H, aromatic); MS (70 eV), *m/e* (relative abundance) 205 (38), 190 (11), 165 (19), 164 (100), 163 (47), 107 (15); IR (CCl<sub>4</sub>) 1435 and 1165 cm<sup>-1</sup>.

Anal. Calcd for C<sub>15</sub>H<sub>11</sub>N: C, 87.77; H, 5.40; N, 6.83. Found: C, 87.46; H, 5.10; N, 6.68.

**Photolysis of DAF in CH<sub>3</sub>CN.** A solution of DAF ( $9.4 \times 10^{-3}$  M) in CH<sub>3</sub>CN was photolyzed at 350 nm in the center of a Rayonet photochemical reactor for 3 h. After evaporation of the solvent, the product mixture was analyzed by <sup>1</sup>H NMR with dioxane as an internal standard and by reverse-phase HPLC (40% H<sub>2</sub>O in CH<sub>3</sub>CN) with 2-methyl-2-phenylpropio[cyclopropane-1,9'-[9H]fluorene] as an internal standard. These procedures revealed the following products: azirine 3 (16%), fluorenone (39%), bifluorenylidene (9%).

**2,3,4-Trimethylspiro[1-pyrroline-5,9'-[9H]fluorene]-cis-3,4-dicarboxylic Acid Anhydride (5).** Diazofluorene (100 mg, 0.5 mmol) and dimethylmaleic anhydride (63 mg, 0.5 mmol) in 25 mL of dry acetonitrile were photolyzed for 4 h in a Vycor tube equipped with a Teflon stopcock under an argon atmosphere at 350 nm. Concentration of the solvent at room temperature on a rotary evaporator and trituration of the residue with cold ether left 20 mg (12%) of a white powder: mp 273–274 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.0 (s, 3 H, methyl), 1.72 (s, 3 H, methyl), 2.43 (s, 3 H, methyl), 6.9–7.8 (m, 8 H, aromatic); IR (CHCl<sub>3</sub>) 1790, 1850 cm<sup>-1</sup>; MS (70 eV), *m/e* (relative abundance) 331 (8), 206 (17), 205 (100), 165 (11), 164 (68), 163 (24), 102.5 (15); molecular ion calcd for C<sub>21</sub>H<sub>17</sub>NO<sub>3</sub>, *m/e* 331.1208; found, 331.1203.

**Spiro[cyclopropane-1,9'-[9H]fluorene]-cis-2,3-dimethyl-2,3-dicarboxylic Acid Anhydride (7).** This compound was prepared by photolysis of  $5 \times 10^{-3}$  M diazofluorene in nitrogen-purged acetonitrile with 0.5 M dimethylmaleic anhydride present with the nitrogen laser (337.1 nm) pulsing at 6 Hz for 40 min. followed by evaporation of the solvent and heating to ca. 80 °C under vacuum to remove by sublimation the excess anhydride. An oily orange solid remained: mp 180–190 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.80 (s, 6 H, methyl) 7.2–7.8 (m, 8 H, aromatic); MS (10 eV), *m/e* (relative abundance) 290 (40), 246 (50), 180 (100), 165 (38); molecular ion calcd for C<sub>15</sub>H<sub>15</sub>O<sub>3</sub>, 290.0943; Found, 290.0943.

**Bis[1-(9-fluorenylideneimine)ethylidene].** This red powder was characterized as a dimeric product from the reaction of nitrile ylide with azirine: UV (CH<sub>3</sub>CN) λ<sub>max</sub> (log ε) 470 (3.0); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 1.90 (s, 6 H, methyl), 7.0–8.2 (m, 16 H, aromatic); MS (70 eV), *m/e* (relative abundance) 410 (54), 245 (30), 206 (12), 205 (35), 180 (14), 165 (57), 164 (100), 163 (38), 149 (16), 78 (20), 44 (70); molecular ion calcd for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>, 410.1783; found, 410.1780.

**General Method of Cyclopropane Synthesis.** Diazofluorene was decomposed catalytically with zinc bromide in neat olefin following the methods developed by Goh, Closs, and Closs.<sup>71</sup> The detailed procedure below is representative of the techniques employed. Following this description, spectroscopic and analytical data for the other cyclopropanes prepared in this manner are summarized.

**2,2-Dimethyl-3-(2-methyl-1-propenyl)spiro[cyclopropane-1,9'-[9H]fluorene].** To a stirred solution of zinc bromide (40 mg, 0.2 mmol) in 15 mL of 2,3-dimethyl-2,4-hexadiene a solution of 150 mg (0.8 mmol) of diazofluorene in 10 mL of the diene was added dropwise over 40 min in the dark. After stirring for 6 h, the reaction mixture was filtered and concentrated at room temperature on a rotary evaporator. The remaining yellow oil was chromatographed on acid-washed alumina eluting with low-boiling petroleum ether, and the crude cyclopropane was then recrystallized from pentane to give 150 mg (55%) (not optimized) of white crystals: mp 138–139 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.38 (s, 3 H, methyl), 2.65 (d, *J* = 5.3 Hz, 1 H, cyclopropyl), 5.5 (m, 1 H, vinyl), 7.2–7.4 (m, 6 H, aromatic), 7.8 (m, 2 H, aromatic); MS (10 eV), *m/e* (relative

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abundance) 274 (52), 259 (67), 244 (24), 231 (100), 229 (29), 217 (85); molecular ion calcd from  $C_{21}H_{22}$ , *m/e* 274.1722; found, 274.1722.

Anal. Calcd for  $C_{21}H_{22}$ : C, 91.92; H, 8.08. Found: C, 91.82; H, 7.97.

**cis-2-Methyl-3-phenylspiro[cyclopropane-1,9'-[9H]fluorene]**: mp 158–160 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.36 (d,  $J = 6.6$  Hz, 3 H, methyl), 2.40 (dq, 1 H, cyclopropyl), 3.50 (d,  $J = 8.1$  Hz, 1 H, cyclopropyl), 6.3–7.7 (m, 8 H, aromatic); MS (10 eV), *m/e* (relative abundance) 282 (100), 267 (77), 265 (22), 192 (24), 165 (19); molecular ion calcd for  $C_{22}H_{18}$ , *m/e* 282.1410; found, 282.1408.

**trans-2-Methyl-3-phenylspiro[cyclopropane-1,9'-[9H]fluorene]**: mp 158–160 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.59 (d,  $J = 6.2$  Hz, 3 H, methyl), 2.15 (dq, 1 H, cyclopropyl), 3.24 (d,  $J = 8.0$  Hz, 1 H, cyclopropyl), 6.2–7.8 (m, 8 H, aromatic); MS (10 eV) *m/e* (relative abundance) 282 (100), 267 (77), 192 (24), 165 (19); molecular ion calcd for  $C_{22}H_{18}$ , *m/e* 282.1410; found, 282.1410.

**trans-2-Methyl-3-ethylspiro[cyclopropane-1,9'-[9H]fluorene]**: mp 68–69 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.85 (t,  $J = 7$  Hz, 3 H, methyl), 1.42 (d,  $J = 6$  Hz, 3 H, methyl), 1.72 (m, 1 H, cyclopropyl), 1.93 (m, 2 H, methylene), 2.15 (m, 1 H, cyclopropyl), 6.9–7.8 (m, 8 H, aromatic); MS (70 eV), *m/e* (relative abundance) 234 (100), 219 (6), 205 (82), 192 (34), 178 (41), 165 (28); molecular ion calcd for  $C_{18}H_{18}$ , *m/e* 234.1409; found, 234.1412.

**2,2,3-Trimethylspiro[cyclopropane-1,9'-[9H]fluorene]**:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.41 (d,  $J = 5.2$  Hz, 3 H, methyl), 14.6 (s, 6 H, methyl), 2.08 (q,  $J = 5.2$  Hz, 1 H, cyclopropyl), 7.2–7.9 (m, 8 H, aromatic).

**cis-2-Methyl-3-ethylspiro[cyclopropane-1,9'-[9H]fluorene]**: mp 63–64 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.91 (t,  $J = 7.2$  Hz, 3 H, methyl), 1.38 (d,  $J = 6.5$  Hz, 3 H, methyl), 1.70 (m, 1 H, cyclopropyl), 1.90 (m, 2 H, methylene), 2.10 (m, 1 H, cyclopropyl); MS (70 eV), *m/e* (relative abundance) 234 (55), 206 (18), 205 (100), 203 (24), 202 (22), 192 (50), 191 (22), 189 (21), 178 (56), 165 (60); molecular ion calcd for  $C_{18}H_{18}$ , *m/e* 234.1409; found, 234.1404.

Anal. Calcd for  $C_{18}H_{18}$ : C, 92.26; H, 7.74. Found: C, 92.31; H, 7.85.

**cis-2,3-Dichlorospiro[cyclopropane-1,9'-[9H]fluorene]**: mp 120–121 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  4.16 (s, 2 H, cyclopropyl), 6.9–7.8 (m, 8 H, aromatic);  $^1H$  NMR (benzene- $d_6$ )  $\delta$  3.76 (s, 2 H, cyclopropyl); IR ( $CCl_4$ ) 1450  $cm^{-1}$ ; MS (70 eV), *m/e* (relative abundance) 262 (5), 260 (8), 227 (33), 226 (17), 225 (100), 190 (17), 189 (59), 188 (7), 187 (11), 165 (20).

Anal. Calcd for  $C_{15}H_{10}Cl_2$ : C, 68.99; H, 3.86; Cl, 27.15. Found: C, 68.82; H, 3.70; Cl, 27.20.

**trans-2,3-Dichlorospiro[cyclopropane-1,9'-[9H]fluorene]**: mp 118–119 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  4.17 (s, 2 H, cyclopropyl), 7.2–7.8 (m, 8 H, aromatic);  $^1H$  NMR (benzene- $d_6$ )  $\delta$  3.47 (s, 2 H, cyclopropyl); IR ( $CCl_4$ ) 1450  $cm^{-1}$ ; MS (70 eV), *m/e* (relative abundance) 262 (6), 260 (8), 228 (5), 227 (33), 226 (16), 225 (100), 190 (16), 189 (54), 188 (6), 187 (11), 165 (5), 95 (12), 94.5 (34), 94 (12), 93.5 (12).

Anal. Calcd for  $C_{15}H_{10}Cl_2$ : C, 68.99; H, 3.86; Cl, 27.15. Found: C, 68.75; H, 4.03; Cl, 27.21.

**Preparation of 9-(2,2-Dichloro-1-ethenylidene)fluorene (10)**. 9-Ethynyl-9-fluorenone<sup>72</sup> (6 g, 30 mmol) was dissolved in 60 mL of anhydrous ether in a 250-mL three-necked flask fitted with a gas inlet frit, Teflon stir bar, and an addition funnel. As HCl gas was slowly bubbled through the reaction mixture, a solution of 12 g (86 mmol) of phosphorous trichloride in 25 mL of anhydrous ether was added dropwise (1 h) with stirring. The reaction mixture was stirred for an additional 2 h with HCl bubbling through it, and then it was cautiously poured over ice. The mixture was neutralized with aqueous NaOH and extracted into ether. The etheral solution was washed with water and saturated NaCl solution, dried over magnesium sulfate, and concentrated on a rotary evaporator. The yellow powder was sublimed and recrystallized from cyclohexane, giving yellow crystals: mp 80–82 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  6.8 (d,  $J = 10$  Hz, 1 H, 7.1–7.8 (m, 9 H)); MS (70 eV), *m/e* (relative abundance) 262 (10), 260 (14), 227 (34), 226 (16), 225 (100), 190 (22), 189 (91), 188 (10), 187 (19), 180 (19), 163 (13), 105 (15), 95 (12), 94 (31), 93 (11).

Anal. Calcd for  $C_{15}H_{10}Cl_2$ : C, 68.99; H, 3.86; Cl, 27.15. Found: C, 69.03; H, 3.76; Cl, 26.87.

**Photolysis Products of Diazofluorene in 6.48 M cis- and trans-1,2-Dichloroethene**. Acetonitrile solutions of diazofluorene ( $2.0 \times 10^{-3}$  M) and *cis*- and *trans*-1,2-dichloroethylene (6.48 M) were prepared, degassed, and photolyzed at 337.1 nm in the normal fashion. The yields of products were determined by analytical reverse-phase HPLC by in-

tegration of peaks monitored at 282 nm and comparison with authentic compounds using an internal standard. Product competition experiments were performed with added methanol (0.2 M), styrene (0.3 M), or diphenyl fumarate ( $3.6 \times 10^{-3}$  M). The stereochemistry of the resulting cyclopropanes was determined by integrating the cyclopropyl hydrogen resonances in the  $^1H$  NMR spectrum after the following workup. After photolysis the sample was concentrated at room temperature on the rotary evaporator, stored in a vacuum desiccator overnight to remove the volatile components of the mixture, and then diluted with benzene- $d_6$ .

**Triplet-Sensitized Irradiation of Diazofluorene**. Two Pyrex cuvettes equipped with magnetic stir bars were filled with a solution of thioxanthone ( $8 \times 10^{-4}$  M), diazofluorene ( $9.2 \times 10^{-4}$  M), and methanol (0.5 M) in acetonitrile. The cuvettes were degassed using four freeze-pump-thaw cycles and then were sealed under vacuum. One of these cuvettes was used as a thermal control. A third cuvette was prepared as above, and additionally included 2,3-dimethyl-2,4-hexadiene (0.05 M) as a triplet quencher (photochemical control). The experimental and photochemical control cuvettes were stirred and irradiated at 380 nm in the sample holder of a Farrand Mark I spectrofluorometer using 10-nm slits. Under these conditions the thioxanthone sensitizer absorbed more than 95% of the incident light. The cuvettes were interchanged every 20 min to ensure equal doses and spent a total of 2.5 h in the beam (sufficient to consume all the diazofluorene present in the experimental cuvette). After irradiation was complete, 1,3,5-triisopropylbenzene was added as an internal standard, and absolute yields were determined by integration of peaks and comparison with injections of authentic 9-methoxyfluorene using a Hewlett-Packard 20-in. 2% OV-101 100-120 WHP column at 130 °C. 9-Methoxyfluorene yields ( $\pm 5\%$ ) were 92% in the experimental sample, 3% in the photochemical control, and 0% in the thermal control.

**Determination of Stereospecificity of Cyclopropanation**. The method described below for the reaction of DAF with *cis*- $\beta$ -methylstyrene is a representative example. A solution of DAF in Freon 113 ( $2.5 \times 10^{-3}$  M) containing *cis*- $\beta$ -methylstyrene (0.56 M) was deoxygenated and irradiated with the nitrogen laser (5 pulses/s at 25 kV, for 45 min). The reaction mixture was evaporated under reduced pressure. The residue was diluted with  $CDCl_3$  and *p*-dioxane was added as an internal standard. The  $^1H$  NMR spectrum of this solution was determined. The yield of cyclopropane, and the ratio of its stereochemical isomers, was determined by integration. Actual experimental reproducibility of this technique is  $\pm 5\%$ .

**Effect of Olefin Concentration on Cyclopropane Stereochemistry**. Acetonitrile solutions of 0.012 M diazofluorene were prepared with varying concentrations of *cis*-2-pentene (2.34–8.18 M). A sample in neat (9.35 M) olefin was also prepared. These samples were deoxygenated in a quartz cuvette equipped with a Teflon stopcock, and each was irradiated for 50 min at 337.1 nm with the nitrogen laser pulsing at 6 Hz. The samples were concentrated at room temperature on a rotary evaporator and kept in a vacuum desiccator overnight to remove volatile components. The stereochemistry of the cyclopropane products was determined by integrating the methyl doublets with the NT-360  $^1H$  NMR in the FT mode. No change in the amount of *cis*-cyclopropane relative to the *trans* isomer was observed over the olefin concentration range examined within our experimental error limit ( $\pm 5\%$ ). Several control experiments were done to check this result. First, the residual olefin from a similarly irradiated sample was analyzed for isomerization. No *trans* olefin could be observed in the mixture by  $^1H$  NMR. Direct irradiation of the cyclopropane could isomerize it;<sup>73</sup> however, it does not absorb light at 337.1 nm. Nevertheless, to ensure that isomerization is not somehow being sensitized by diazofluorene, or any of the noncyclopropane side products, a solution of diazofluorene ( $8.6 \times 10^{-3}$  M), authentic *cis*-cyclopropane ( $7.9 \times 10^{-3}$  M), and styrene (1.0 M) in acetonitrile was prepared, irradiated, and analyzed as above. None of the *trans*-cyclopropane could be detected.

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**Registry No.** 3, 16504-40-8; 5, 87319-54-8; 6, 83693-17-8; 7, 87319-55-9; 9, 87319-61-7; 10, 87319-65-1; DAF, 832-80-4; F1, 2762-16-5; diethyl fumarate, 623-91-6; diethyl mesoxalate, 609-09-6; fumaronitrile,

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764-42-1; methyl acrylate, 96-33-3; acrylonitrile, 107-13-1; maleic anhydride, 108-31-6; methanol, 67-56-1; ethanol, 64-17-5; isopropanol, 67-63-0; diphenyl fumarate, 6338-19-8; *trans*-1,3-pentadiene, 2004-70-8; styrene, 100-42-5; *trans,trans*-2,4-hexadiene, 5194-51-4; 2,5-dimethyl-2,4-hexadiene, 764-13-6; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; trimethylethylene, 513-35-9; cyclohexene, 110-83-8; *trans*-1,2-dichloroethylene, 156-60-5; *cis*-propenylbenzene, 766-90-5; *cis*-1,2-dichloroethylene, 156-59-2; *trans*-propenylbenzene, 873-66-5; acetonitrile, 75-05-8; dimethyl maleic anhydride, 766-39-2; bis[1-(9-fluorenylidene)

imine]ethylidene], 87319-56-0; 2,2-dimethyl-3-(2-methyl-1-propenyl)-spiro[cyclopropane-1,9'-(9*H*)fluorene], 87319-57-1; *cis*-2-methyl-3-phenylspiro[cyclopropane-1,9'-(9*H*)fluorene], 87319-58-2; *trans*-2-methyl-3-phenylspiro[cyclopropane-1,9'-(9*H*)fluorene], 87319-59-3; *trans*-2-methyl-3-ethylspiro[cyclopropane-1,9'-(9*H*)fluorene], 87319-60-6; *cis*-2-methyl-3-ethylspiro[cyclopropane-1,9'-(9*H*)fluorene], 87319-62-8; *cis*-2,3-dichlorospiro[cyclopropane-1,9'-(9*H*)fluorene], 87319-63-9; *trans*-2,3-dichlorospiro[cyclopropane-1,9'-(9*H*)fluorene], 87319-64-0; 9-ethynyl-9-fluorenone, 13461-74-0; cyclohexane, 110-82-7.

## Kinetics and Mechanism of the Interaction of Potassium Peroxydisulfate and 18-Crown-6 in Aqueous Media

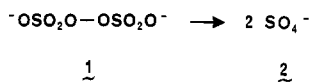
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**Abstract:** A kinetic investigation of the interaction of potassium peroxydisulfate with the crown ether 18-crown-6 in basic aqueous media has shown that the crown ether has a tremendous accelerating effect upon the rate of disappearance of peroxydisulfate. This acceleration is due in part to a radical chain mechanism in which crown is oxidized, and which is similar to that observed in the presence of simple ethers. However, an additional crown effect is observed which is explicable in terms of a Coulombic attraction between a cation-complexed crown radical and the peroxydisulfate dianion.

Potassium peroxydisulfate is well known as a free radical initiator in emulsion polymerization reactions<sup>1</sup> and as an oxidant in aqueous media.<sup>2</sup> More general utilization of this relatively inexpensive peroxide has been limited, perhaps, due to the fairly high activation energy (33.5 kcal/mol in basic media<sup>3</sup>) for homolytic scission of the peroxidic linkage. A more serious deterrent to its use is its general insolubility in organic solvents and only modest solubility (5.3 g/100 cm<sup>3</sup> at 20 °C<sup>4</sup>) in aqueous media.

We recently reported<sup>5</sup> that phase transfer catalysts allow utilization of peroxydisulfate as a polymerization initiator in organic media. The surprising efficiency of these "phase transfer free radical polymerizations" led us to speculate<sup>6</sup> that a "naked" peroxydisulfate (**1**) might be expected to exhibit enhanced tendencies toward fragmentation to sulfate radical anions (**2**) because of increased Coulombic repulsion between the anionic termini of "naked" **1**.



In order to assess this question, we decided to investigate the kinetics of the thermal decomposition of aqueous potassium peroxydisulfate in the presence of the crown ether 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6).<sup>7</sup> Peroxydisulfate reaction kinetics have been studied extensively in aqueous media in both the absence<sup>3</sup> and presence<sup>8</sup> of ether ad-

Table I. Influence of Temperature and Additives on Rate of Decomposition of Potassium Peroxydisulfate<sup>a</sup>

temp, °C	additive	<i>k</i> (L/mol s)	<i>E<sub>a</sub></i> (kcal/mol)	ln <i>A</i>	Δ <i>S</i> <sup>‡</sup> (cal/mol deg)
40	18-crown-6 <sup>b</sup>	1.65 × 10 <sup>-2</sup>	19.9	31.9	2.6
45	18-crown-6 <sup>b</sup>	2.25 × 10 <sup>-2</sup>			
50	18-crown-6 <sup>b</sup>	4.02 × 10 <sup>-2</sup>			
55	18-crown-6 <sup>b</sup>	6.45 × 10 <sup>-2</sup>			
60	18-crown-6 <sup>b</sup>	1.08 × 10 <sup>-1</sup>			
50	diglyme <sup>c</sup>	3.78 × 10 <sup>-3</sup>	29.0	43.8	25.8
60	diglyme <sup>c</sup>	2.18 × 10 <sup>-2</sup>			
70	diglyme <sup>c</sup>	5.01 × 10 <sup>-2</sup>			
50	none <sup>d,e</sup>	1.1 × 10 <sup>-6</sup>	33.5 <sup>f</sup>	43.4 <sup>g</sup>	25.5 <sup>g</sup>
50	none <sup>d</sup>	1.0 × 10 <sup>-6</sup> <sup>f</sup>			

<sup>a</sup> [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]<sub>0</sub> = 0.01 M. <sup>b</sup> 0.12 M. <sup>c</sup> 0.24 M. <sup>d</sup> First-order reaction, units of *k* are s<sup>-1</sup>. <sup>e</sup> This work. <sup>f</sup> Reference 3. <sup>g</sup> Calculated from the data given in ref 3.

Table II. Dependence of Initial Rates on Peroxydisulfate Concentration

[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] (mol/L)	I.R. (mol/L s)
2.5 × 10 <sup>-3</sup>	8.0 × 10 <sup>-7</sup>
4.8 × 10 <sup>-3</sup>	3.6 × 10 <sup>-6</sup>
7.1 × 10 <sup>-3</sup>	7.1 × 10 <sup>-6</sup>
9.7 × 10 <sup>-3</sup>	1.3 × 10 <sup>-5</sup>

ditives. Although the concept of "naked" ions is seldom considered in the highly solvating medium, water, the rather limited solubility of potassium peroxydisulfate compared to that of the closely analogous salts potassium sulfate (12 g/100 cm<sup>3</sup> at 25 °C<sup>4</sup>) and ammonium peroxydisulfate (58.5 g/100 cm<sup>3</sup> at 0 °C<sup>4</sup>) suggested to us a possible lack of total ionic dissociation and thus a potential source of a crown effect.

The present report details our kinetic investigations of the dramatic accelerating effect that 18-crown-6 has on the rate of

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