acid-catalyzed reaction of diphenylphosphine and benzaldehyde.[20] Our method is by far the mildest one available, as it is anhydrous and avoids strong acids, bases, and oxidizing agents, making it the one of choice for complex molecules,[24] which are likely to contain functionality sensitive to at least one of these conditions. The other results in Table II show that this new reaction is also useful for dialkyl ketone trisylhydrazones, especially methyl ones, provided there is no α branching. Such selectivity can be a desirable feature.

Aliphatic and aromatic six-membered rings are common in natural as well as man-made substances, and this new reaction will undoubtedly prove useful in the synthesis of such compounds. The diphenylphosphinoyl group is becoming an important activating group in organic synthesis,[18,25] which adds to the significance of this new addition reaction of arenesulfonylhydrazones.

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Radical-Like Reactions of Singlet Fluorenylidene. Hydrogen and Halogen Abstraction[1]

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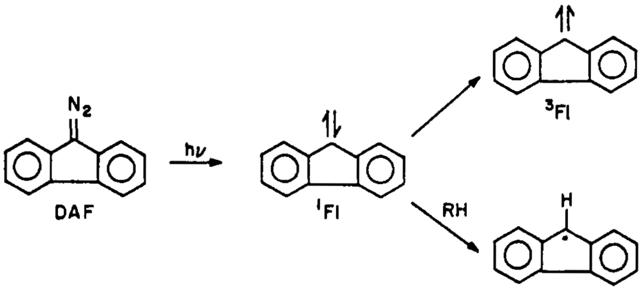
During the last few years there have been several reports of absolute rate constants[2] for the reactions of carbenes in solution.[3-6] Most recently, Zupancic and Schuster have reported rate constants for the reactions of singlet (^{1}Fl) and triplet (^{3}Fl) fluorenylidene with a variety of olefins[7] as well as activation parameters for intersystem crossing.[8] However, in these studies a major reaction pathway for the decay of ^{1}Fl was not included in the mechanism proposed when acetonitrile was used as solvent, namely, that ^{1}Fl readily abstracts hydrogen from the solvent to give the 9-fluorenyl radical. This reaction has a significant bearing on the interpretation of the kinetic data.



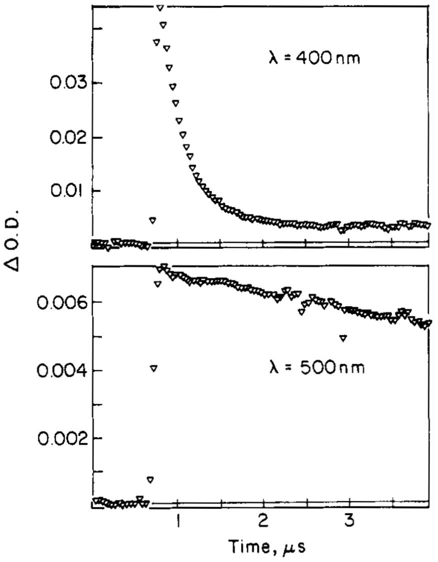


Figure 1. Traces obtained at 400 and 500 nm in the presence of diethyl fumarate (0.025 M). Conditions: T = 300 K, [DAF] = 0.008 M, solvent: acetonitrile.

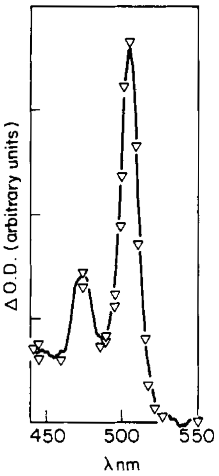


Figure 2. Absorption spectrum of the 9-fluorenyl radical in benzene solvent at 25 °C. Continuous trace was obtained by a modulation spectrometer. The point spectrum was obtained by laser flash photolysis. The two spectra have been overlapped for ease of comparison.

Laser flash photolysis of diazofluorene (DAF; 8×10^{-4} M) in acetonitrile leads, as was previously reported,[7] to the formation of a short-lived transient (λ_{max} 470 nm; lifetime = 27 ns) which is assigned to ^{1}Fl.[9] As this species decays, two other bands are produced at λ_{max} 400 (broad) and 500 nm (very sharp) for which the lifetime of *formation* is 27 ns (in good agreement with the *half-life* of 17 ns reported by Schuster[7]), indicating that these bands are derived from ^{1}Fl decay. As a result of this observation and by comparison with earlier literature reports,[7,8] both bands were assigned to ^{3}Fl which was formed with high efficiency and the lifetime observed was found to represent the kinetics for intersystem crossing, i.e., $^1\text{Fl} \rightarrow {}^3\text{Fl}$. However, if ^{1}Fl decayed to give two different products, each will *necessarily* be formed with the same lifetime, which is in fact the case in this instance.[11] This agreement between the decay rate at 470 nm and the buildup profiles at 400 and 500 nm is observed under a variety of con-

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(1) Issued as NRCC No. 19620.

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ditions, which include solvent and temperature changes, as well as addition of quenchers such as cyclohexane (vide infra). These observations provide conclusive proof that the 400 and 500-nm transients are products resulting from reactions of the 470-nm species.

When the above experiment is repeated in the presence of diethyl fumarate (0.025 M) or oxygen, the same two bands are formed, but each decays with different kinetics (see Figure 1, where the ratio of lifetimes for the two bands is 10) and hence cannot be assigned to the same species. In the presence of diethyl fumarate the transient at 400 nm decays more rapidly, suggesting that the assignment of ^{3}Fl is correct, while in the presence of oxygen the converse is true. This suggests that the 500-nm transient may be due to the 9-fluorenyl radical. Indeed, it is the only transient formed from ^{1}Fl decay if the photolysis is carried out in cyclohexane which serves as a good hydrogen donor.

The assignment of the 500-nm peak (and its characteristic 470-nm shoulder band) was confirmed by generating the 9-fluorenyl radical independently. Thus, photolysis of di-*tert*-butyl peroxide in a benzene solution containing fluorene using either laser flash photolysis or modulation spectroscopy[12,13] for detection gives the same spectrum in the 500-nm region as is observed in the photolysis of DAF (Figure 2).

When DAF is photolyzed in CD_3CN at 27 °C, the lifetime of ^{1}Fl is 37 ns as compared with 27 ns for CH_3CN as solvent, an effect which we believe is due to a deuterium isotope effect on the abstraction process. If we assume that the isotope effect is infinitely large, we can obtain a *lower* limit of 27% for the extent to which ^{1}Fl is converted to the fluorenyl radical in acetonitrile. Hence, hydrogen abstraction by ^{1}Fl is an important reaction pathway even in a fairly inert solvent.

A rough estimate of the importance of hydrogen abstraction in acetonitrile can also be obtained by using the signals in cyclohexane as a relative actinometer. If we assume that under these conditions abstraction is quantitative (no other transient detected), then, by comparing the optical densities due to fluorenyl radical in both solvents, we estimate that abstraction accounts for 20–35% of the ^{1}Fl decay in acetonitrile. When small amounts of cyclohexane were added to a solution of DAF in CD_3CN, we observe a gradual increase in the yield of the 500-nm transient relative to that of ^{3}Fl (which remained long lived), as well as a decrease of the lifetimes associated with the processes at 400, 470, and 500 nm. The lifetimes measured (e.g., 14 ns for 0.46 M cyclohexane at 30 °C) were wavelength independent, as expected, and thus rule out the possibility that the radical could be formed in this time scale from the long-lived ^{3}Fl or a short-lived excited-state precursor. From a plot of the reciprocal of the ^{1}Fl lifetime vs. cyclohexane concentration, we estimate k(cyclohexane) = 8.3×10^{-7} M^{-1} s^{-1} at 30 °C.[14]

Further, evidence for the radical like behavior of ^{1}Fl was obtained by photolyzing DAF (8×10^{-4} M) in carbon tetrachloride at 27 °C. The transient absorption spectrum due to ^{3}Fl could not be detected but a sharp peak at 490 nm with a shape virtually identical with that recorded for the fluorenyl radical was formed, which is assigned to the 9-chlorofluorenyl radical. As support for this assignment, we and others[15] have isolated 9,9′-dichloro-9,9′-bifluorenyl in ca. 50% yield. Moreover, typical carbene scavengers such as diethyl fumarate have little or no effect on the lifetime of this transient.

An important consequence of the role of hydrogen abstraction by ^{1}Fl is that its lifetime cannot be regarded as a measure of the rate constant for intersystem crossing.[8] The observed rate constants for singlet decay represent a composite due to intersystem crossing and hydrogen abstraction.

Measurements of the rate constants over the temperature range −40 to +60 °C in CH_3CN and CD_3CN can be represented, respectively, by the expressions 1 and 2, where $\theta = 2.3RT$ kcal

$$\log k/\mathrm{s}^{-1} = 9.64 \pm 0.10 - (2.85 \pm 0.13)/\theta \qquad (1)$$

$$\log k/\mathrm{s}^{-1} = 9.23 \pm 0.25 - (2.47 \pm 0.29)/\theta \qquad (2)$$

mol^{-1} and the errors correspond to 95% confidence limits. These expressions do not yield Arrhenius parameters directly since they cannot be assigned to elementary steps in the decay of ^{1}Fl. However, since in CH_3CN the ratio[17] of the signals at 400 and 500 nm changes from 7.1 at 57 °C to 9.1 at −40 °C, we can conclude[18] that 2.85 kcal mol^{-1} represents a lower limit for the activation energy of hydrogen abstraction and an upper limit to that for intersystem crossing.

Finally, it should be noted that hydrogen abstraction from the solvent by ^{1}Fl does not affect the conclusions regarding the kinetics of the reactions of ^{1}Fl with olefins. Our values for the activation energies and log A values for reaction of ^{1}Fl with two olefins based on direct, time-resolved experiments in CD_3CN are in good agreement with those published for other olefins.[18] For diethyl fumarate and 2,3-dimethylbutene, we obtained activation energies of 0.29 and 1.93 kcal mol^{-1} and log A/M^{-1} s^{-1} values of 9.37 and 10.23, respectively.[19]

Acknowledgment. Thanks are due to S. E. Sugamori for his technical assistance and also to Dr. C. Huggenberger and Professor H. Fischer for generously sharing the design for their modulation spectrometer.

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[16] The activation energy for deuterium abstraction can be expected to be higher than for hydrogen; however, the apparent activation energy is smaller in acetonitrile-d_3 because the relative importance of abstraction decreases (with a concurrent increase in intersystem crossing which tends to decrease E_a).

[17] This ratio cannot be used directly to determine the difference in activation energy between the two processes because of the possibility of some underlying absorption by ^{3}Fl.

[18] A value of 1.9 kcal mol^{-1} was previously obtained as the apparent activation energy for singlet decay,[8] from measurements over a smaller temperature range. This lower value was incorporated in competition studies into activation energies for quenching of ^{1}Fl by olefins and led to negative activation energies for the latter reactions.[8]

[19] The experimental data obtained in this work were corrected to allow for the increase in concentrations which occurs as the solutions contract on cooling.

Carbenes and the O–H Bond: Cyclopentadienylidene and Cycloheptatrienylidene

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A variety of carbenes react with alcohols to give ethers.[1] The mechanism of these "O–H insertions" has not received much attention. At least three plausible reaction paths are conceivable: (a) One-step insertion into the O–H bond (comparable to the C–H insertion of singlet carbenes), (b) electrophilic attack of the carbene at oxygen, followed by proton transfer, and (c) protonation of the carbene to give a carbocation (or ion pair) (Scheme I). The electrophilic vs. nucleophilic character of the carbene should play a major role in selecting the proper mechanism. Cyclo-

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