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Registry No. Papain, 9001-73-4; *N*-benzoylimidazole, 10364-94-0.

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A Critical Examination of Transient Assignments in the Laser Flash Photolysis of 9-Diazofluorene[1]

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Laser photolysis of 9-diazofluorene (DAF; 1×10^{-3} M) in acetonitrile yields a transient species with λ_{max} 470 nm, which decays with first-order kinetics and has a lifetime of 27 ns at room temperature.[2,3] The decay of this transient leads to two new absorption bands at 400 and 500 nm.[2,3] In their original study of this system, Zupancic and Schuster assigned the absorption at 470 nm to singlet fluorenylidene, ^{1}Fl, while those at 400 and 500 nm were assigned to the triplet carbene, ^{3}Fl.[2] Further experiments based on these assignments led to the unusual conclusion that singlet fluorenylidene added nonstereospecifically to olefins.[4]

Experiments carried out in this laboratory[3] showed that the original assignment of the 500-nm absorption to ^{3}Fl was incorrect and that it was in fact due to the 9-fluorenyl radical. On further investigation, we have found that the original assignments[2] of the other bands also require revision. We conclude that the absorption at 470 nm was due to ^{3}Fl while that at 400 nm was due to an ylide formed in the reaction of fluorenylidene with acetonitrile. Singlet fluorenylidene was not detected, presumably because its lifetime was shorter than 10 ns.

Laser flash photolysis (337.1 nm, ~8 ns, up to 10 mJ, 300 K) of DAF in a variety of solvents showed that the buildup of the 400-nm band concurrent with the decay at 470 nm was only observed with nitrile solvents. It was therefore highly unlikely that the 400-nm band was due to ^{3}Fl. In hexafluorobenzene, for example, we measured a lifetime of 95 ns for the 470-nm band. The transient was quenched rapidly when cis-4-methyl-2-pentene was added, and the rate constant was found to be 2.1×10^8 M^{-1} s^{-1}. This result can be combined with a report by Jones and Rettig[5] to show that the 470-nm transient was in fact *triplet* fluorenylidene, rather than the singlet carbene as was originally reported.[2]

Jones and Rettig showed that when DAF was photodecomposed in hexafluorobenzene and *cis*-4-methyl-2-pentene mixtures containing from 5 to 100 mol % olefin, the degree of stereoselectivity in the cyclopropane products[6] was concentration dependent. Our laser experiments show that their lowest concentration was sufficient to quench over 90% of the 470-nm species. There would then be no reason for the ratio of any two products of reaction (such as the cyclopropanes) to be concentration dependent, *regardless of whether singlet addition is stereospecific or not*. A reasonable explanation for these data is that the 470-nm transient is not the singlet but instead the triplet carbene. The reason for the changes in stereoselectivity with olefin concentration should be attributed to the involvement of the shorter lived singlet carbene, which becomes trappable only a high olefin concentrations. Since the singlet carbene is trappable, yet undetectable by nosecond techniques, its lifetime must be between 0.05 and 5 ns.

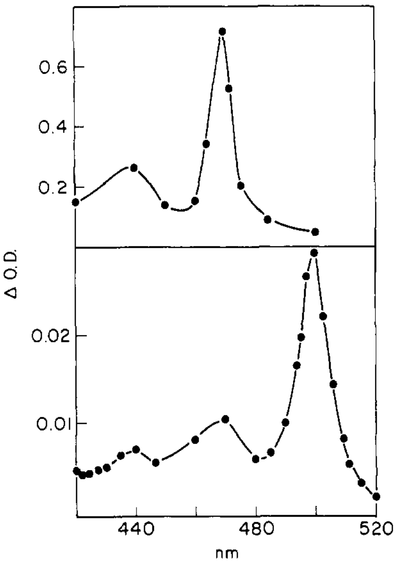

Figure 1. Transient spectra obtained during the laser flash irradiation of 10^{-3} M DAF in a 1:1 isopentane:diethyl ether glass at 77 K (top), and spectrum of the 9-fluorenyl radical obtained by attack of *tert*-butoxyl radicals (from peroxide photodecomposition) on fluorene at 300 K (bottom).

In support of this assignment, we have found that laser flash photolysis of DAF (1×10^{-3} M) in an isopentane:diethyl ether glass at 77 K led to the transient absorption at 470 nm, which had a lifetime of ca. 80 μs.[7] The band at 470 nm consisted of two components separated by ~1360 cm^{-1} (Figure 1). The form and separation of the maxima were virtually identical with those observed for the 9-fluorenyl and 9-chlorofluorenyl radicals.[3] This supports the assignment of the 470-nm absorption band to triplet fluorenylidene since diarylcarbenes and their corresponding radicals have similar electronic configurations and are therefore likely to have similar absorption spectra.[8]

Much of the case for the original, incorrect, assignment[2] of the band at 400 nm to ^{3}Fl was based on a comparison of that absorption with carbene absorption spectra in matrices reported by Closs. However, in his work[9] Closs only described details of the spectrum due to diphenylmethylene; that due to ^{3}Fl has not been reported. We believe that the 400-nm buildup, observed in nitrile solvents (acetonitrile, acetonitrile-d_3, pivalonitrile, and benzonitrile), must be due to reaction of fluorenylidene with nitriles,[10] presumably leading to an ylide, by analogy with reactions involving ketones.[12]

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(1) Issued as NRCC publication no. 20598.

(2) Zupancic, J. J.; Schuster, G. B., *J. Am. Chem. Soc.* **1980**, *102*, 5958; *Ibid*, **1981**, *103*, 2423.

(3) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 5934.

(4) Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 944.

(5) Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013.

(6) We have found that in this reaction fluorenylidene also adds to hexafluorobenzene and that the adduct is formed in ca. 20% yield. Laser photolysis also indicates that some hydrogen abstraction takes place, presumably at the allylic site. Professor M. Jones Jr. has recently repeated and confirmed the results published in ref 5. He has found little product formation association with the abstraction process. We are grateful to Professor Jones for his willingness to undertake these experiments.

(7) This may not have been the maximum lifetime attainable at this temperature since our monitoring light may have caused some softening of the matrix.

(8) Trozzolo, A. M.; Gibbons, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 239

(9) Closs, G. L.; Hutchinson, C. A., Jr.; Kohler, B. *J. Chem. Phys.* **1966**, *44*, 413.

(10) The absorption spectra of nitrile ylides trapped in matrices have been previously reported.[11]

(11) Sieber, W.; Gilgen, P.; Chaloupka, S.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 1679. Orhavots, A.; Heimgartner, H.; Schmid, H. *Ibid.* **1975**, *58*, 2662. Padwa, A. *Acc. Chem. Res.* **1976**, *9*, 371.

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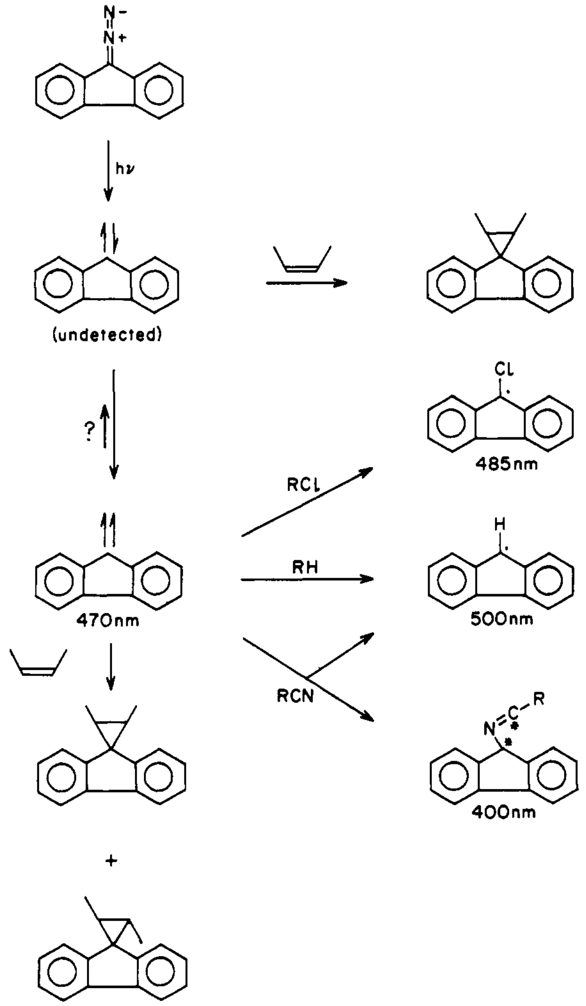
Scheme I



The above interpretation is supported by product studies (using GC–MS analysis) that show two major products on similar yields (ca. 20% each). One was 9-fluorenylacetonitrile, expected from radical recombination following abstraction from the solvent. The second product incorporates the acetonitrile moiety bonded at the nitrile center and indicates direct attachment of the carbene on the solvent. The mass spectrum of a third and minor product indicates incorporation of two acetonitrile moieties, in excellent agreement with the mechanism recently proposed by Kende et al.[13] Thus, nitriles should be regarded as highly reactive rather than "inert" solvents as was originally suggested.[2] The revised mechanism proposed for the reactions of fluorenylidene is shown in Scheme I.

Further confirmation that transients at 400 nm were nitrile ylides was obtained from olefin quenching experiments. Thus, fumaronitrile quenches the acetonitrile ylide with $k_q = (5.7 \pm 0.4) \times 10^7$ M^{-1} s^{-1}. By contrast, when pivalonitrile was used, we obtained $k_q = (1.5 \pm 0.2) \times 10^7$ M^{-1} s^{-1} under the same conditions.[14]

Thus, fluorenylidene is a highly reactive carbene that reacts with solvents containing hydrogen or chlorine to give the 9-fluorenyl radical and with ketones or nitriles to form ylides. Since ylides typically have singlet ground states, the interesting question arises as to whether they can be formed directly from the triplet carbene. Although simple mechanism ultimately leading to the singlet ylide can be advanced for such a process, it is possible that singlet and triplet fluorenylidene are in equilibrium.[16] However, our results require that for $^1Fl \rightleftarrows {}^3Fl$, $K \geq 10$ and that quenching by *cis*-4-methyl-2-pentene was competitive with intersystem crossing.

The above reassignments fit all of the available data and the behavior of the carbene conforms to the normally accepted reaction mechanisms. They account for (i) nonstereospecific additions to olefins,[4] (ii) radical-like behavior in atom abstractions,[3] giving good yields of cage escape, (iii) spectral similarities between the 470-nm band and the 9-fluorenyl radical,[3] (iv) dramatic enhancement of the lifetime measured at 470 nm at 77 K, (v) buildup of transients at 400 nm only when nitriles were present and with their ylide-like properties such as preferred reaction with electron deficient olefins,[11] and (vi) formation of several products containing acetonitrile moieties in the photolysis of DAF in acetonitrile.

Finally, most of the data in earlier reports can be reinterpreted on the basis of this revised mechanism. Results involving the 400-nm transient should be assigned to a nitrile–ylide. Time-resolved data for the 470-nm species correspond to triplet fluorenylidene or species (singlet?) in equilibrium with it. Conclusions concerning carbene intersystem crossing should be ignored. Results based on a reduction of the quantum yield of the formation of the 400-nm transient (earlier assigned to singlet fluorenyidene) should be treated cautiously; such a reduction may reflect quenching of the singlet, triplet, or both, before or after equilibration.

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[13] Kende, A. S.; Hebeisen, P.; Sanfilippo, P. J.; Toder, B. H. *J. Am. Chem. Soc.* **1982**, *104*, 4244.

[14] Our earlier measurements[15] of these rate constants were repeated to ensure the match of experimental conditions with the experiments described below.

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[16] A condition that is believed to be met in the case of diphenylcarbene.[17,18]

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Irradiation of Diazofluorene on a Picosecond Time Scale and at Very Low Temperature: A Reassignment of Transient Structures

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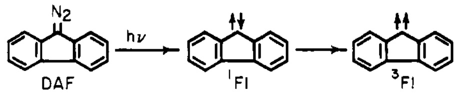
Irradiation of 9-diazofluorene (DAF) leads to loss of nitrogen and eventual formation of products characteristic of the reactions of singlet fluorenylidene (^{1}Fl) and triplet fluorenylidene (^{3}Fl); eq 1).[1] Irradiation of DAF with a 10-ns light pulse permits detection



(1)

of transient products. Three significant products are observed in acetonitrile solution at room temperature.[2,3] The first is produced during the pulse, absorbs at 470 nm, and decays with a half-life of 17 ns. The second product grows in as the first decays, absorbs at 400 nm, and has a half-life of about 100 μs. Also, a small amount of 9-fluorenyl radical (FlH·), which has a unique absorption at 500 nm, appears as the first product decays.[3] Previously we assigned the 470- and 400-nm absorbing products to ^{1}Fl and ^{3}Fl, respectively.[2] Irradiation of DAF in cyclohexane solution with a 10-ns pulse shows only FlH·.[2,3] Herein we report

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[1] Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013; 4015.

[2] Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 5958.

[3] Wong, P. C.; Griller, D.; Scaiano, J. *J. Am. Chem. Soc.* **1981**, *103*, 5934.

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