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Fluorenylidene: Kinetics and Mechanisms

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Abstract: Laser irradiation of 9-diazofluorene in solution leads to the formation of a transient species with λ_{max} = 470 nm that has been characterized as the triplet carbene and is believed to be in thermal equilibrium with the singlet state, which lies within a few kcal/mol. The singlet carbene is frequently more reactive and tends to dominate the chemistry. For example, in hydrogen donors, the triplet state abstracts hydrogen leading to the 9-fluorenyl radical, which is the only species detected in the flash experiments. However, product studies demonstrate that the predominant reaction path is the insertion of the singlet into C–H bonds (e.g., in cyclohexane), a process that is transparent to the technique of nanosecond laser photolysis. Irradiation of 9-diazofluorene in nitrile solvents results in carbene addition to the nitrile function, leading to nitrile ylides that react rapidly with electron-deficient olefins and present a characteristic absorption band at ~400 nm. The singlet carbene has a lifetime of ≤5 ns and obeys the Skell–Woodworth rules.

The chemistry of diarylcarbenes, and of fluorenylidene in particular, has been the subject of extensive investigation. Most of the activity before 1980 focused on product studies and spectroscopic investigations of matrix-isolated carbenes.[4] Kinetic studies have traditionally been concerned with the measurement of relative rate constants for carbene reactions. In a pioneering study, Closs and Rabinow[5] demonstrated that flash photolysis techniques could be used to measure absolute rate constants for the reactions of diphenylcarbene. This approach has recently been extended to laser flash photolysis studies on diphenylcarbene,[6–11] arylchlorocarbenes,[12–15] fluorenylidene,[16–22] 1-naphthylcarbene,[23] and dimesitylcarbene.[24]

The potential of laser flash photolysis in the study of carbene reactions was quickly recognized; unfortunately, the limitations of the technique were only discovered by trial and error. Schuster and Zupancic,[16] in their original laser flash photolysis investigation of fluorenylidene in acetonitrile solvent, reported the observation of three transient absorption bands. These were assigned to singlet fluorenylidene (470 nm) and triplet fluorenylidene (400, 500 nm). Work in our laboratories has demonstrated that all of these assignments were incorrect and has provided suitable reassignments for all bands.[19,20] More recent work from Schuster's laboratory agrees well with our band assignments.[21]

Much of the recent work on fluorenylidene, particularly from our own and Schuster's laboratories, has been published in communication form. From an experimental point of view, all of these publications are in full agreement where they overlap; however, several of these reports contain incorrect assignments or interpretations and quite frequently insufficient experimental detail to make a critical reevaluation of the data.

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[1] National Research Council of Canada.
[2] The Ohio State University.
[3] Issued as NRCC-22935.
[4] E.g.: Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. Moss, R. A., Jones, M., Jr., Eds. "Carbenes"; Wiley, New York, 1973; Vol. 1, 2.
[5] Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190–8198.
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[12] Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576–7578.
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[14] Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549–5551.
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[19] Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6631–6635.
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[24] Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1984**, *106*, 543.

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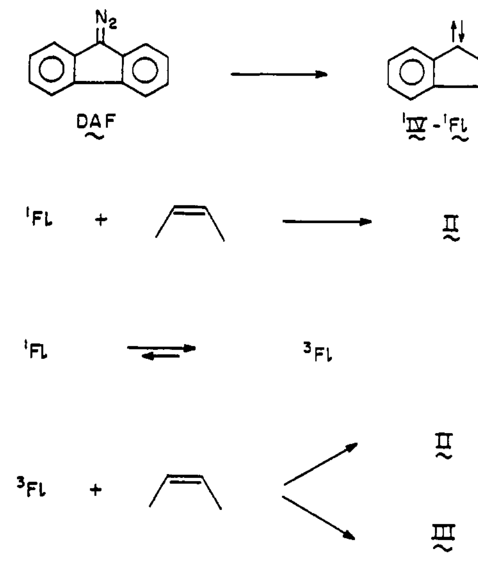
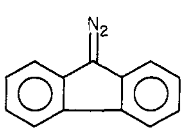
Scheme I



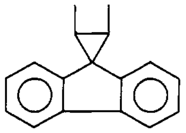
In this paper we wish to report a detailed and complete analysis of the data on fluorenylidene. It is important to emphasize that laser photolysis techniques do not necessarily monitor the main or most abundant transient, but in most cases merely those transients giving the strongest signals. Furthermore, the species detected is not necessarily the one responsible for the reaction decay processes monitored, but in fact any species in equilibrium with it can yield results that can be indistinguishable from the major chemistry of the species monitored. Understanding this is critical in carbene chemistry where questions of singlet–triplet equilibration and stepwise vs. concerted mechanisms are commonplace.

The data reported herein include a considerable number of results from laser flash photolysis techniques, complemented by experiments involving product studies, matrix isolation spectroscopy, and EPR spectroscopy in matrices. Combined, they allow a rather detailed understanding of the chemistry of fluorenylidene, which, more often than not, strongly supports the ideas that had been derived from traditional product and scavenging studies.

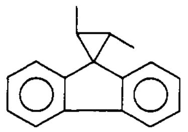
Previous Chemical Studies of Fluorenylidene. A most important mechanistic investigation of fluorenylidene was due to Jones and Rettig.[25a] In this now classic work the chemistry of singlet and triplet fluorenylidene was elucidated by chemical trapping studies. Irradiation of 9-diazofluorene (I) (DAF) in *cis*-2-butene yields cis and trans cyclopropanes II and III in roughly a 2:1 ratio. The cyclopropanes are formed in 50% yield and account for 80–90% of the addition products. Dilution with hexafluorobenzene leads to a steady reduction in II/III. At the highest dilution, 95 mol % hexafluorobenzene, this ratio was 0.3. A very similar dilution effect was observed with *cis*-4-methyl-2-pentene as quencher.



I (DAF)



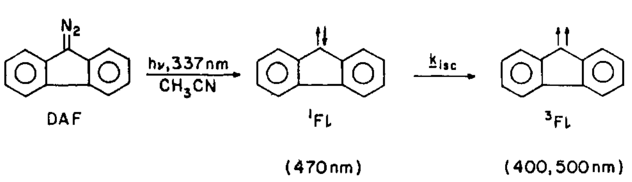
II



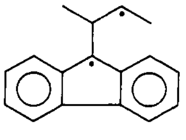
III

These observations were most reasonably interpreted in terms of a cascade mechanism (Scheme I) and application of the Skell–Woodworth hypothesis.[26] Photolysis of DAF leads to loss of nitrogen and formation of singlet fluorenylidene, ^{1}Fl. The singlet carbene can react concertedly with olefin with maintenance of stereochemistry to give cis spirocyclopropane II. In competition with cyclopropanation, ^{1}Fl can intersystem cross to the triplet ^{3}Fl, which is known to be the ground state by EPR.[27] The triplet reacts with olefin in a stepwise manner to give triplet biradical V, which then gives a mixture of cis and trans cyclopropanes. Dilution with hexafluorobenzene slows down the rate of the bimolecular process without affecting unimolecular ISC and therefore increases the yield of trans cyclopropane.

Scheme II[a]



[a] Assignments according to ref 16.



V

Jones and Rettig[25a] obtained strong evidence in support of their mechanism by scavenging fluorenylidene simultaneously with 1,3-butadiene and *cis*-2-butene. The chemistry of ^{3}Fl is analogous to a free radical addition to a double bond. One expects that the rate of this process will depend upon substituents on the olefin that will stabilize the incipient radical center of the biradical. A corresponding rate enhancement is not expected in the singlet manifold as this is a concerted process. Experimentally, the photolysis of DAF in 11.5 M 1,3-butadiene and 3.0 M *cis*-2-butene gives a ratio of II/III of 49. This is more than 20-fold larger than the value obtained in neat *cis*-2-butene. 1,3-Butadiene has selectively scavenged ^{3}Fl, effectively demonstrating that singlet ^{1}Fl obeys the Skell–Woodworth hypothesis.[26]

Early Flash Photolysis Work on Fluorenylidene. The pioneering work on the laser flash photolysis of DAF was performed by Zupancic and Schuster.[16,17] Nitrogen laser photolysis of DAF in acetonitrile gave a transient at 470 nm within the time resolution of the experiment (5 ns). The 470-nm band decayed with a half-life of 17 ns and was replaced by new bands at 400 and 500 nm. Zupancic and Schuster assigned the first observed species to be ^{1}Fl and the latter bands as due to ^{3}Fl (Scheme II). The former observation was quite exciting for it marked the first direct detection of a singlet carbene in the condensed phase. The evidence in favor of these assignments was principally (i) that the 470-nm species reacted very rapidly with expected singlet carbene quenchers such as methanol and simple alkenes ($k = (3–9) \times 10^8$ $M^{-1}\ s^{-1}$) and (ii) that the 400- and 500-nm transient spectrum was identical with a previously reported matrix spectrum of ^{3}Fl.[28] The species assigned as ^{3}Fl reacts very sluggishly or not at all with methanol, styrene, isoprene, and simple olefins but quite rapidly with electron-poor alkenes such as maleic anhydride, diethyl fumarate, and fumaronitrile.[16,17,22] This reactivity pattern was somewhat disturbing as the work of Jones and Rettig indicated that ^{3}Fl should react readily with conjugated dienes.[25a] Laser photolysis of DAF in alkane solvents gave a transient at 497 nm which is formed instantaneously on the time scale of the experiment. The latter band was assigned as the 9-fluorenyl radical. The authors offered two explanations: a large solvent effect on carbene reactivity or hydrogen atom abstraction by an excited state of DAF.[16]

These assignments led Zupancic and Schuster to several remarkable conclusions.[16,17] The rate constant for the reaction of

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(25) (a) Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013–4015. (b) We thank Professor Jones for pointing out that the 1:1 adduct detected by GC/mass spectroscopy most likely had a cycloheptatriene structure.

(26) Woodworth, R. C.; Skell, P. S. *J. Am. Chem. Soc.* **1959**, *81*, 3383–3386.

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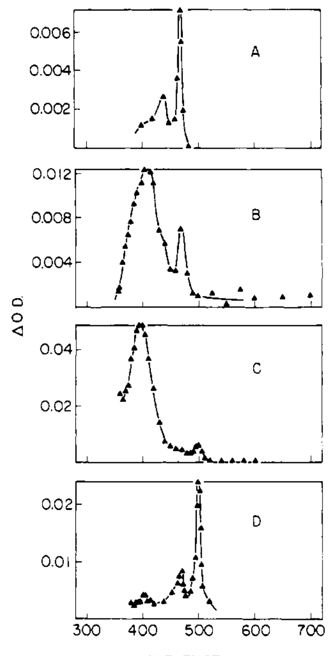


Figure 1. Transient spectra obtained by laser flash photolysis of DAF under various conditions: (A) in a diethyl ether, isopentane glass at 77 K, monitored about 1 μs after excitation; (B) in acetonitrile at 300 K, monitored at the end of the laser pulse and for about 15 ns (note that the average over this period already favors the 400-nm ylide band); (C) similar to B, but monitored between 1 and 3 μs after excitation, the band at 500 nm corresponds to the 9-fluorenyl radical; (D) in cyclohexane at 300 K, monitored between 1 and 3 μs after excitation. The intensity of all the spectra are not directly comparable since only B and C were obtained the same day, and day-to-day variations in sensitivity are common.

the 470-nm species with *cis*-2-pentene was determined to be 1.29 × 10^8 M^{-1} s^{-1}. According to these assignments photolysis of DAF in the presence of 4.45 M *cis*-2-pentene should lead to 93% capture of nascent ^{1}Fl before ISC to ^{3}Fl. However, the products formed from this photolysis mixture consisted of 53% cis cyclopropane and 33% trans cyclopropane. A very similar pattern was observed with *cis*-2-methylstyrene. It was concluded that singlet fluorenylidene adds to cis olefins with considerable loss of stereochemistry,[17] in violation of the Skell–Woodworth rules,[26] and in contradiction to the *cis*-2-butene, 1,3-butadiene product studies of Jones and Rettig.[25a]

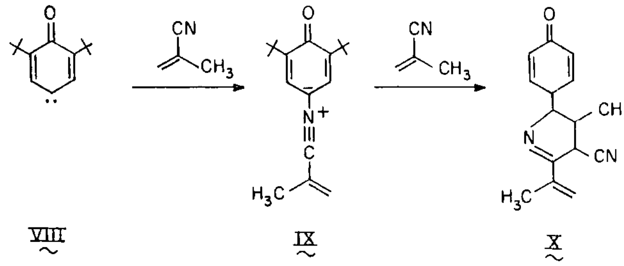
These observations also question the basis of the dilution effect observed by Jones and Rettig. Assuming that the rate constant of *cis*-2-butene and *cis*-2-methyl-4-pentene are similar to that of *cis*-2-pentene, ^{1}Fl should be 100% trapped in neat olefin, and ^{1}Fl should be trapped in over 90% efficiency at the lowest dilution used by Jones and Rettig.[25a] No dilution effect should have been observed, regardless of whether singlet reaction is stereospecific.[20]

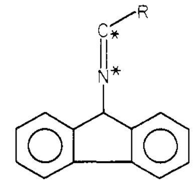
The assignments of the transient spectra obtained from photolysis of DAF were soon amended by Wong, Griller, and Scaiano.[18] These workers noted that although the 400- and 500-nm bands are formed at the same apparent rate, they have different lifetimes and different reactivities toward various quenchers. The 500-nm band, originally thought to be ^{3}Fl, was in fact due to the 9-fluorenyl radical. On further investigation the original assignments of the other two bands were also found to require revision.[20] The conclusion reached was 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. These assignments are completely consistent with chemical studies and are detailed in the next section.

Results and Discussion

(A) Detection of Ylides by Laser Flash Photolysis. Laser flash photolysis of DAF in a number of relatively inert solvents led to the decay of a band at 470 nm. In solvents such as acetonitrile, however, a second band at 400 nm is observed, whose buildup is concurrent with the decay at 470 nm. Laser flash experiments in other nitrile solvents, benzonitrile and pivalonitrile, also lead to a transient absorption band very similar to that observed in acetonitrile, Figure 1C. It is therefore reasonable to assign the 400-nm band as nitrile ylide VI, rather than triplet fluorenylidene.

Scheme III





VIa, R = CH_3
b, R = $C(CH_3)_3$
c, R = C_6H_5

Absorptions in the 400-nm region are occasionally observed in other solvents, but usually they are not formed concurrently with the decay at 470 nm, and the peak does not match that in acetonitrile.[29] In the case of benzonitrile the spectrum of VIc is essentially the same as that observed in aliphatic nitriles, but the signals are substantially weaker, suggesting that the scavenging pathways detected with other aromatics (presumably addition) are also available to this substrate. Further support for this assignment comes from the fact that different ylides are derived from different nitrile solvents and correspondingly react with different rate constants with the same quenchers.[30] Specifically, fumaronitrile reacts with VIa with k_q = (5.7 ± 0.4) × 10^7 M^{-1} s^{-1}, but VIb reacts with the same quencher with k_q = (1.5 ± 0.2) × 10^7 M^{-1} s^{-1} under the same conditions. The reaction of triplet fluorenylidene with fumaronitrile would not be expected to show such a large solvent dependence.

The assignment of 400 nm as a nitrile ylide resolves many of the chemical problems associated with labeling this band triplet fluorenylidene. Nitrile ylides are not expected to show radical-like reactivity with hydrogen atom donors such as toluene or to undergo radical-like addition reactions with styrene or isoprene. On the other hand, the chemical trapping studies of Huisgen,[31] Padwa,[32] and Schmid[33] all indicate that nitrile ylides should react rapidly with electron-poor olefins. This is exactly the pattern of reactivity observed for the 400-nm band.

In retrospect the reaction of a carbene with a nitrile to form a nitrile ylide is neither unusual nor surprising. In 1979 Magee and Shechter[34] proposed a nitrile ylide intermediate VII from the reaction of 5-*tert*-butyl-3*H*-pyrazolylidene with benzonitrile to explain the high yield of ortho substitution. Sheppard et al. soon

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(29) For example, in C_6F_6 a signal with λ_{max} ~ 450 nm is also produced, formally instantanously, and is very long lived in the time scale of typical ^{3}Fl experiments. The origin of this intermediate is not entirely clear, although it does not seem to have any significant effect on the spectroscopic or kinetic properties of the 470-nm band.

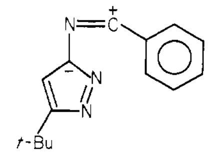
(30) The same transient has now been detected in the 308-nm laser photolysis of the corresponding azirene: Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufman, K. J.; Schuster, G. B., personal communication.

(31) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633–645.

(32) Padwa, A. *Acc. Chem. Res.* **1976**, *9*, 371–378.

(33) E.g.: Orahovats, A.; Heimgartner, H.; Schmid, H.; Heinzelmann, W. *Helv. Chim. Acta* **1975**, *58*, 2662–2667.

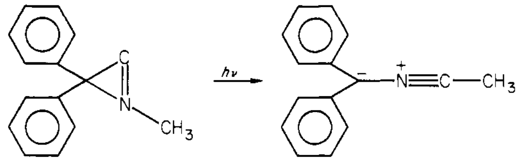
(34) Magee, W. L.; Shechter, H. *Tetrahedron Lett.* **1979**, 4697–4700.



VII

after also proposed a nitrile ylide derived from reaction of a heterocyclic carbene with nitrile.[35]

In 1982 Kende et al.[36a] reported the formation of a nitrile ylide from carbenes and methacrylonitrile. The relevant part of Kende's mechanism is shown in Scheme III. The closely related nitrile ylide XII has been generated by photolysis of azirene XI in a glassy matrix at 77 K. Schmid demonstrated that this is UV active with λ_{max} = 355 nm.[33]



XI XII

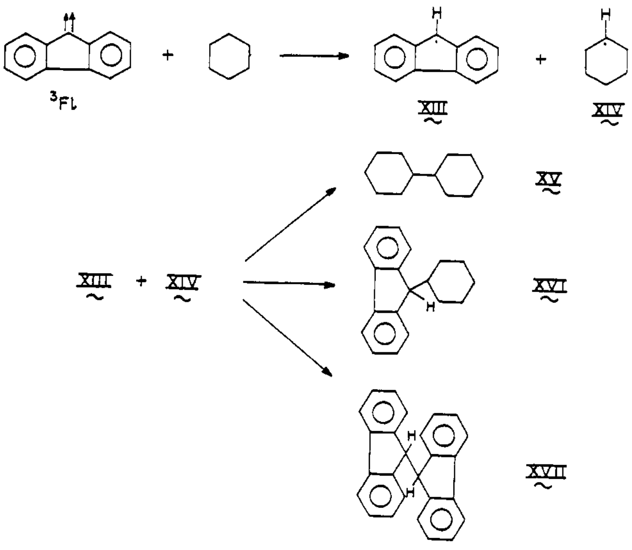
The nitrile ylide formed by reaction of 1-naphthylmethylene with acetonitrile has recently been generated from three different sources: reaction of the carbene derived from either diazo compound or diazirene, as well as by ring opening of the corresponding azirine; the same transient, absorbing at 386 nm, was observed in all cases.[36b]

The reaction of carbenes with heteroatoms bearing a lone pair of electrons to give ylides has been discussed for years.[31-33] Carbonyl ylides derived from ketones and carbenes have been detected by laser flash photolysis,[19] as well as in the direct photolysis of oxiranes.[37] deMarch and Huisgen[38] have recently reported chemical evidence for carbonyl ylides derived from bis(methoxycarbonyl)carbene.

Much of the case in favor of the original assignment of the 400-nm band as triplet fluorenylidene was based on a comparison with a low-temperature matrix spectrum reported by Closs.[28] However, in his work Closs only described the absorption spectrum of diphenylcarbene. Prior to the original laser flash studies reported in 1980 there was no published matrix spectrum of triplet fluorenylidene in the literature.

There is a common perception that ground-state triplet carbenes such as fluorenylidene are indefinitely stable in typical organic glasses at 77 K. This perception is correct only under certain very narrow conditions. To detect the carbene, it is necessary to employ very high concentrations of diazo precursor (1 M) and a very inert matrix such as hexafluorobenzene. Triplet fluorenylidene is not stable at 77 K under the conditions of high dilution usually associated with optical spectroscopy. In fact, one can barely detect triplet fluorenylidene by EPR during continuous irradiation of a 10^{-3} M solution of DAF in methylcyclohexane glass at 77 K. Within 1–2 min after the light is turned off the EPR signal has decayed by irreversible reaction with the matrix. We have found that a rather convenient way of obtaining the spectra is by combining matrix isolation with laser photolysis techniques. Thus, laser photolysis of DAF in a glass from a 1:1 mixture of diethyl ether and isopentane yields a well-resolved spectrum with λ_{max} = 470 nm, which was identical with the species produced "instantaneously" in flash experiments at room temperature (Figure 1A). The lifetime of the 470-nm band (the formation of which is essentially instantaneous under these conditions) was at least 80 μs. Singlet to triplet ISC is not expected to show a large temperature dependence,[39] therefore the 470-nm band is most likely triplet fluorenylidene. Schuster[21] has found that the 470-nm band is indefinitely stable in 2-methyltetrahydrofuran at 10 K, and has consequently reassigned this species as ^{3}Fl. The 470-nm band consisted of two components separated by 1360 cm^{-1}. The form and separation of the maxima were virtually identical with those observed for the 9-fluorenyl and 9-chlorofluorenyl radicals.[18,20] 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.[40,41]

Scheme IV



Assignment of the 470-nm band as triplet rather than singlet fluorenylidene resolves the conflict between the laser flash and chemical trapping studies. It is no longer surprising that the carrier of this band can undergo radical-like atom-transfer reactions.[18] There is no violation of the Skell–Woodworth rules, as the rate constant of singlet fluorenylidene with olefins must be considerably larger than those attributed to the 470-nm band.[17] To account for the dilution effect observed by Jones and Rettig[25a] and recognizing that the upper limit of singlet reactivity with olefins is the diffusion rate, we predict that the singlet lifetime must be in the range of 0.05 to 5 ns.[20] Indeed, in more recent work Schuster has found that the 470-nm band ^{3}Fl is formed with a time constant of 0.41 ns,[21] in acetonitrile solvent.

(B) Product Studies. Product studies in the case of fluorenylidene (and presumably other carbenes) are complicated mainly by two factors: first, carbenes readily react with their diazo precursors, with rate constants that may approach diffusion control. Second, fluorenylidene is extremely reactive toward most solvents, making it difficult to find conditions under which reaction with the solvent can be largely avoided. To further complicate the problem, it is not unusual for these reactions to yield photolabile products; in this sense, it is important to note that the fluorene group is a very good chromophore.

The high reactivity toward the diazo precursor means that from a practical point of view experiments have to be carried out in very dilute solutions, frequently submillimolar, and the products concentrated after irradiation of large volumes.

(C) Photochemistry in Cyclohexane. In cyclohexane, as in several other good hydrogen-donor solvents, the only transient detected in flash experiments is the 9-fluorenyl radical (vide infra).

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(36) (a) Kende, A. S.; Hebeisen, P.; Sanfilippo, P. J.; Toder, B. H. *J. Am. Chem. Soc.* **1982**, *104*, 4244–4245. (b) Barcus, R. L.; Wright, B. B.; Platz, M. S.; Scaiano, J. C. *Tetrahedron Lett.* **1983**, *24*, 3955–3958.

(37) Trozzolo, A. M.; Leslie, T. M.; Sarpotdar, A. S.; Small, R. D.; Ferraudi, G. J.; DoMinh, T.; Hartless, R. L. *Pure. Appl. Chem.* **1979**, *51*, 261–270.

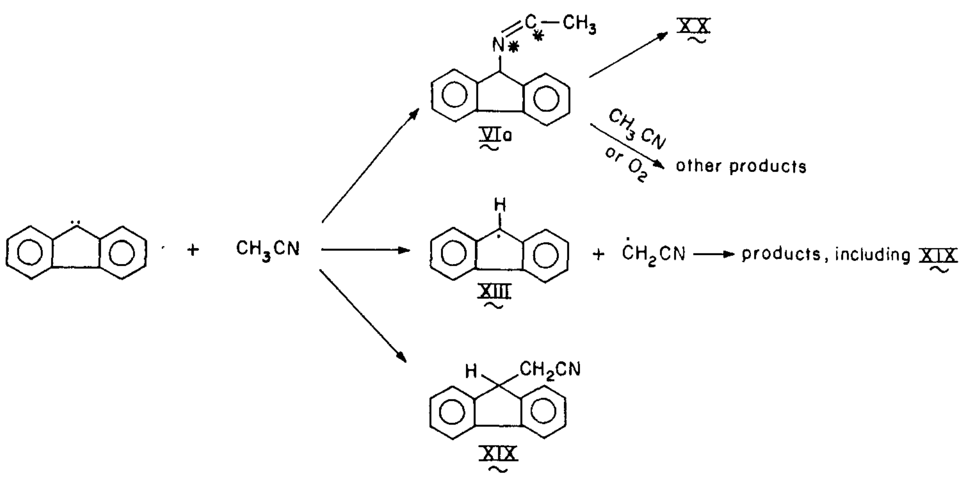
(38) Huisgen, R.; deMarch, P. *J. Am. Chem. Soc.* **1982**, *104*, 4953–4954.

(39) The temperature dependence for intersystem crossing has been reported for 1-pyrenylnitrene: Sumitani, M.; Nagakura, S.; Yoshihara, K., *Bull. Chem. Soc. Jpn.*, **1976**, *49*, 2995–2998.

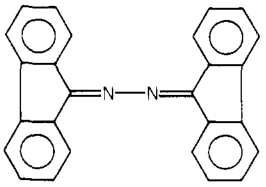
(40) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329–335.

(41) Trozzolo, A. M.; Gibbons, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 239–243.

Scheme V

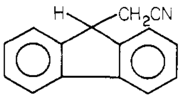


This makes this system a particularly interesting one from the point of view of product studies, since, if the predominant chemistry is the one detected in flash experiments, the products should be those typical of radical processes, according to the mechanism of Scheme IV. For the sake of simplicity, we have included in Scheme IV only the reactions leading to combination products; however, it should be noted that some disproportionation is also expected, particularly in the self-reaction of cyclohexyl.[42] Much to our surprise the main product of the reaction between fluorenylidene and cyclohexane was XVI. The following relative yields were obtained in 10^{-3} M DAF solution: XV 0.13%, fluorene 7.8%, XVI 65.4%, XVII 9.4%. The cross-combination ratio based on this data would be ~3500, a very different value from the expected ratio of 4 for free radical process. Quite clearly, the difference is beyond any error that could have been introduced by neglecting the disproportionation of cyclohexyl. Even taking this disproportionation into account, one can estimate that at most 14% of XVI arises from free radical processes. Fluorene ketazine (XVIII) was also present, as it is in almost all preparative experiments involving fluorenylidene, and results from reaction of the carbene with its diazo precursor.

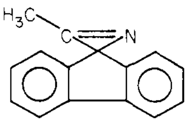


XVIII

Photolysis of DAF in Acetonitrile. These reactions led to four products containing acetonitrile moieties (see Experimental Section). Two isomers have been characterized as **XIX** and **XX**, each one corresponded to ca. 25% of the nitrile-containing products. XIX is expected from combination of 9-fluorenyl radicals (XIII) with $\dot{C}H_2CN$, which results from abstraction from the solvent. XX is the product of ring closure of the ylide VIa. A third product contained two acetonitrile moieties and may be the result of reactions similar to those recently reported by Kende et al.[36] The remaining product appeared to be an oxide of XX, presumably due to residual oxygen or to oxidation during handling of the reaction mixture.

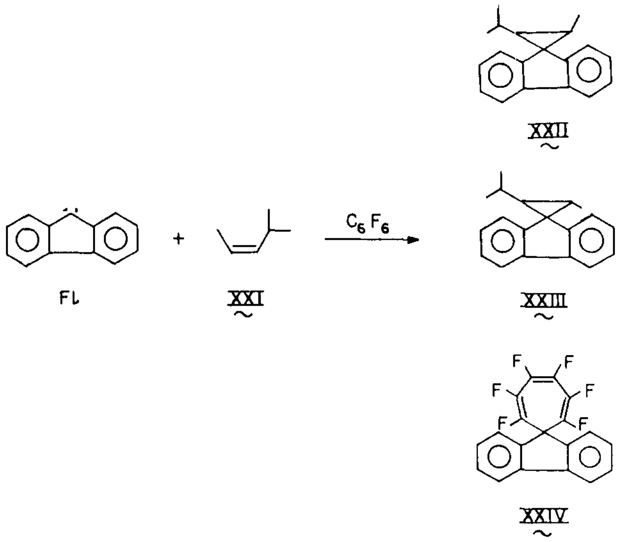


XIX



XX

Scheme VI



The products of the photolysis of DAF in acetonitrile are thus consistent with a mechanism leading mainly to the corresponding ylide, XIa, which can subsequently lead to several products via cyclization, further reactions with the solvent, or presumably reaction of VIa with oxygen. The yields of XIX suggest an upper limit of about 20% for the hydrogen abstraction reaction pathways, although consideration of the results in cyclohexane suggests that a good fraction, if not most, of XIX may arise from nonradical pathways. Scheme V summarizes the proposed reactions. As usual, some fluorene ketazine (XVIII) was also detected.

Reaction of Fluorenylidene with *cis*-4-Methyl-2-pentene. Our experiments in this area largely confirm those reported in 1965 by Jones and Rettig.[25a] As indicated in an earlier communication,[20] our experiments also reveal the addition of fluorenylidene to hexafluorobenzene used as a solvent.[25b] Scheme VI shows the products of reaction observed. At hexafluorobenzene concentrations of 72 and 52 mol % the respective ratios of XXII/XXIII were 0.29 and 0.43 in good agreement with published results.[25a] These results are entirely consistent with the trapping of two transients, presumably singlet and triplet carbene, which at least at the higher olefin concentrations are not in equilibrium. The results do not provide any information as to whether the two states are in equilibrium or not in the absence of olefin, although all other experiments seem to indicate that this is indeed the case. An analysis of this type does not require the assumption that the singlet reaction is stereospecific but rather that singlet and triplet reactions yield cyclopropanation products in different ratios.

No products arising from hydrogen abstraction–recombination reactions could be detected, even when laser photolysis experiments (vide infra) indicate that some allylic abstraction does take place.

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[42] Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441–464.

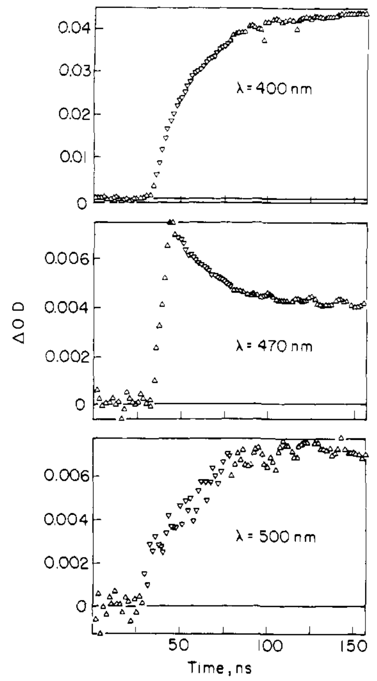


Figure 2. Traces obtained monitoring the transient signals at 400, 470, and 500 nm for a solution of DAF in acetonitrile at 300 K.

Table I. Lifetime of Triplet Fluorenylidene (470 nm) under Different Experimental Conditions

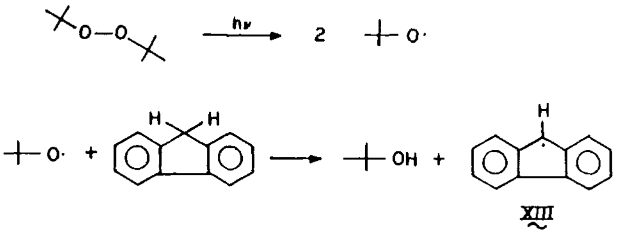
solvent	τ/ns	T/K	notes
acetonitrile-d_3	38.7	300	$E_a = 2.47 \pm 0.29^a$ $\log A = 9.23 \pm 0.25^b$
acetonitrile	27	300	$E_a = 2.85 \pm 0.09^a$ $\log A = 9.64 \pm 0.07^b$
$C_6F_5CF_3$	98	300	
C_6F_6	96	300	
C_6H_5Cl	23	200	
$Me_3COOCMe_3$	29	293	at 500 nm
	94	239	at 500 nm
CH_2Cl_2	31	245	at 500 nm
Freon-113	290	300	at 482 nm
isopentane	55	191	470 and 500 nm

[a] In kcal/mol. [b] With A in unit of s^{-1}.

(D) Laser Flash Photolysis. All experiments in this section have been carried out using 337.1-nm pulses from a nitrogen laser for excitation. Laser photodecomposition of DAF in moderately inert solvents systematically leads to the formation of the transient absorbing at 470 nm as the first detectable species. The transients that follow and that are formed concurrently with the decay of ^{3}Fl depend upon the nature of the environment and the experimental conditions used.

Decay of Triplet Fluorenylidene (470 nm). We have been unable to find any solvent that we can truly describe as inert towards ^{3}Fl. Perfluorinated aliphatic hydrocarbons may conceivably be sufficiently "inert"; however, DAF is essentially insoluble in them, a fact that effectively renders them useless. As a result, the decay of fluorenylidene in most solvents is controlled by its reactions with the media. The lifetime of ^{3}Fl can be monitored either at 470 nm (direct analysis of the decay) or at a wavelength where a product of reaction is generated, such as 400 nm in nitrile solvents or 500 nm in hydrogen donors (vide infra). In some solvents, such as acetonitrile, the three wavelengths are suitable for kinetic analysis, and the same lifetime can be obtained at 400, 470, or 500 nm. Figure 2 shows representative traces obtained at all three wavelengths in acetonitrile. Table I summarizes the lifetime values under various experimental conditions. In the case of Freon-113, the growth of the 9-chloro-9-fluorenyl radical was monitored at 482 nm. While this is the solvent in which we obtained the longest lifetime, the radical and the triplet carbene are too close (482 and 470 nm, with a weaker band at shorter wavelengths in each case) to be convenient for detailed studies.

Scheme VII



In the case of acetonitrile and acetonitrile-d_3, the decay of the triplet was examined in the 233–333 K range and the corresponding Arrhenius parameters have also been included in Table I.

As pointed out earlier, the characterization of the 9-fluorenyl radical as a product of the reaction of Fl with many solvents has played an important role in understanding the behavior of this carbene under laser excitation. The following section details the results that lead to the unequivocal assignment of the 500-nm transient to the 9-fluorenyl radical.

Characterization of the 9-Fluorenyl Radical. The 9-fluorenyl (XIII) radical was characterized in several experiments which conclusively show that the 500-nm band, and a weaker band/shoulder at ~470 nm, are due to this species. The latter is frequently responsible for the residual absorbance observed when the decay of triplet fluorenylidene is monitored at this wavelength; i.e., the traces do not return to the original or prepulse level.

Photodecomposition of di-*tert*-butyl peroxide in the presence of fluorene yields the 9-fluorenyl radical according to the reactions in Scheme VII.

The transient spectrum obtained reveals the characteristic band at 500 nm, along with some triplet fluorene, easily characterized by its band at 380 nm.[43] Interestingly, triplet fluorenylidene and the 9-fluorenyl radical show the same band structure (compare Figure 1A,D), a similarity that has been pointed out by Trozzolo[40] for other carbenes and supports the assignments presented herein.

The signals from 9-fluorenyl radical were also characterized by modulation spectroscopy with the reactions in Scheme VII as the source.[44]

There are several solvents in which the only species we could detect by flash photolysis was the 9-fluorenyl radical; e.g., isopentane, cyclohexane (Figure 1D), and tetrahydrofuran (THF) at room temperature. For THF, even at 180 K, the formation of the radical was so fast that we could not unambiguously time resolve the process.

In carbon tetrachloride the only species detected showed a maximum at 485 nm and has been characterized as the 9-chloro-9-fluorenyl radical.

Reaction with Nitriles. Fluorenylidene readily reacts with nitriles in a process that, according to the product studies described previously, clearly involves addition at the C≡N center. Hydrogen abstraction also takes place and is substantially reduced in acetonitrile-d_3, as expected.

In the laser experiments, the reaction with nitriles leads to a strong absorption band at 400 nm. This band is now recognized as due to a nitrile ylide. The presence of this band has been confirmed in acetonitrile, acetonitrile-d_3, pivalonitrile, and benzonitrile. Figure 1B,C illustrates the spectra obtained at different time delays. In acetonitrile the formation of the 500-nm signal due to 9-fluorenyl is concurrent with (though much weaker than) the production of the 400-nm band. In benzonitrile no 500-nm signal was observed, a fact that is consistent with the absence of abstractable hydrogens in this solvent; the 400-nm band is rather weak in this solvent, presumably as a result of carbene reactions with the aromatic ring since similar "carbene loss" situations have

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(43) Porter, G.; Windsor, M. W. *Proc. R. Soc. London, Ser. A* **1958**, *245*, 283–258.

(44) For a description of the technique and instrumentation used see: Marriott, P. R.; Castelhano, A. L.; Griller, D. *Can. J. Chem.* **1982**, *60*, 274.

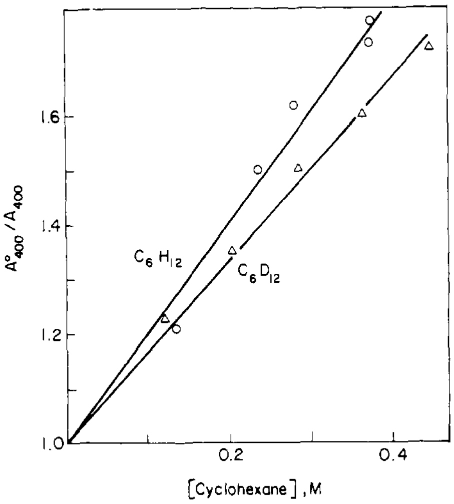

Figure 3. Stern–Volmer plot for the quenching of the 400-nm signal by cyclohexane and cyclohexane-d_{12}, in acetonitrile-d_3 at 300 K.

been observed in other aromatic solvents. For example, in benzene no significant signals are detected.

We note that the temperature dependence given in Table I for the decay of triplet fluorenylidene in acetonitrile and acetonitrile-d_3 should be attributed to carbene reactions with the solvent. Further, since this decay results from a composite of several reaction paths (vide infra), the use of an Arrhenius expression should be merely regarded as a convenient but arbitrary way of reporting the temperature dependence.

Reaction with Hydrogen Donors. As pointed out above, fluorenylidene will abstract hydrogen atoms from a wide range of substrates, some of which (such as acetonitrile or acetone) would not be normally considered good hydrogen donors.

In a few cases we have been able to measure the rates of reaction of the carbene with hydrogen donors. For example, in the case of cyclohexane in acetonitrile-d_3, we obtained $k_q = 8.3 \times 10^7$ M^- s^{-1} at 300 K from a time-resolved study of the decay of the 470-nm band. Once again, it should be emphasized that rate constants measured in this manner will include *all* reaction paths between triplet fluorenylidene and cyclohexane, as well as a weighted component from any reaction of a species in equilibrium with triplet fluorenylidene. In the case of singlet carbene reactions, the weighting factor will be mainly determined by the corresponding equilibrium constant (vide infra).

An alternative approach to the determination of kinetic constants is the use of a Stern–Volmer type of technique. That is, by use of a simplified reaction mechanism $k_q\tau$ can be obtained from eq 1, where $A_{400}{}^0$ and A_{400} are the experimental transient

$$A_{400}{}^0/A_{400} = 1 + k_q\tau[Q] \qquad (1)$$

absorptions at 400 nm in the absence and presence of the quencher Q, respectively. It is further assumed that *only* the ylide is responsible for the signals at this wavelength. An additional assumption, which will be presented in some more detail later, is that no ylide is formed prior to singlet–triplet equilibration; the absence of a "jump" in the 400-nm signals suggests that this assumption is correct.

Equation 1 is directly applicable to systems involving only one transient intermediate or where more than one intermediate is involved, but they are and remain in equilibrium for all quencher concentrations.

Using the approach described above, we obtain $k_q\tau$ values of 2.03 and 1.68 M^{-1} for cyclohexane and cyclohexane-d_{12}, respectively, in acetonitrile-d_3 at 300 K. The isotope effect calculated from this data is $k_H/k_D \sim 1.2$. Figure 3 illustrates the corresponding plots.

Examination of the relative yields of 9-fluorenyl and 9-fluorenyl-*9-d* radical in neat cyclohexane and cyclohexane-d_{12} at 300 K lead to an isotopic ratio of yields of 1.0 ± 0.15; unfortunately, this type of measurement is typically subject to errors of this magnitude.[45] Possible interpretations of this small value include a role for proton transfer in the insertion reaction or an insertion mechanism based on an in-cage abstraction–recombination process or a very exothermic reaction with a highly asymmetric transition state.

Table II. Quenching of Fluorenylidene by Hydroxylic Substrates at 300 K

solvent	quencher	$k_q{}^a$	$k_q\tau_T$,^{b} M^{-1}
C_6F_6	CH_3OH^d	$(6.30 \pm 1.23) \times 10^8$	
	CH_3OD	$(4.59 \pm 0.85) \times 10^8$	
	CD_3OH	$(7.48 \pm 1.56) \times 10^8$	
	CD_3OD	$(5.25 \pm 0.69) \times 10^8$	
acetonitrile-d_3	CH_3OH		32.6 ± 3.8
	CH_3OD		23.5 ± 1.3
Cl_4C	CH_3OH		0.75
acetonitrile-d_3	CH_3COOH		21.6 ± 3.8^c

^{a} Time resolved in units of M^{-1} s^{-1}. ^{b} Stern–Volmer analysis of the data. ^{c} Slow (4×10^6 M^{-1} s^{-1}) quenching of the ylide observed. ^{d} An independent measurement yields $(5.7 \pm 0.9) \times 10^8$ M^{-1} s^{-1}.

Quenching experiments with toluene in acetonitrile yield $k_q\tau = 1.73$ M^{-1}. However, it should be noted that very little 500-nm signal (9-fluorenyl) was observed in this system.

Reaction with Hydroxylic Substrates. The kinetics of these reactions were examined using the same approach described in the previous section, and the rates obtained are subject to the same limitations regarding their interpretation. The 9-fluorenyl radicals are not detected in any of these systems when the quencher concentration is large enough to scavenge all the carbene. The kinetic data obtained have been summarized in Table II. Significant quenching of the ylide itself (400-nm band) was observed in the case of acetic acid (see Table II).

It is clear that deuteration of the methyl group in methanol has no effect on the rates of reaction. The effect of deuteration at the hydroxylic position is less clear. There seems to be a well-defined variation leading to $k_H/k_D \sim 1.4$; however, examination of the error limits (reported always as $\pm 2\sigma$) shows that its significance is somewhat borderline. We note that these measurements are rather difficult due to the intrinsically short lifetimes involved and leave little scope for improvement on the data in Table II.

Reaction with Unsaturated Compounds. All our measurements in this area were carried out by use of time-resolved techniques and essentially the same approach discussed in the sections above. In a few cases we also examined the effect of temperature on the quenching.

The experiments with *cis*-4-methyl-2-pentene in perfluorobenzene solvent were planned so as to ensure that the experimental conditions used matched those in the preparative experiments described earlier and with the data reported by Jones and Rettig.[25]

Again, the use of Arrhenius expressions to report the temperature dependence should only be regarded as a convenient format and in no way taken to mean that the data reflect a single elementary reaction step. The results have been summarized in Table III.

It should be noted that in the case of *cis*-4-methyl-2-pentene we have detected some 9-fluorenyl radical in the laser experiments; however, product studies indicate that cyclopropanation is the predominant reaction path, and no products (<2%) from radical processes were detected. The yield of 9-fluorenyl was substantially lower in the case of 2-methyl-2-pentene, presumably as a result of the absence of tertiary allylic hydrogen and the faster overall kinetics.

Reaction with Carbonyl Compounds. These processes have been reported in considerable detail in an earlier publication[18] and will not be repeated here. It is sufficient to say that reaction of

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(45) Essentially isotope-insensitive ratios have also been observed by others (Grasse, P. B. Ph.D. Thesis, University of Illinois, Urbana, IL, 1982). We are grateful to Prof. G. B. Schuster for bringing these experiments to our attention.

Table III. Quenching of Fluorenylidene by Olefins at 300 K

solvent	substrate	$k_q(300\ K)^a$	$E_a{}^b$	$\log A^c$	range, K
C_6F_6	*cis*-4-methyl-2-pentene	$(2.1 \pm 0.5) \times 10^8$			
C_6F_6	2-methyl-2-pentene	$(7.7 \pm 1.7) \times 10^8$			
acetonitrile-d_3	2,3-dimethylbut-2-ene	$(5.1 \pm 0.6) \times 10^8$	1.93	10.23	265-303
acetonitrile-d_3	diethyl fumarate	$(1.5 \pm 0.3) \times 10^9$	0.29	9.37	233-334

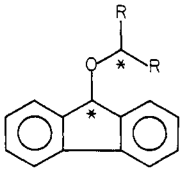
[a] Units of $M^{-1}\ s^{-1}$. [b] Units of kcal/mol. [c] With A in units of $M^{-1}\ s^{-1}$.

Table IV. Reactivity of Nitrile Ylides toward Various Olefins[a]

ylide	quencher	$k/M^{-1}\ s^{-1}$	$\log (A/M^{-1}\ s^{-1})$	E_a/kcal mol^{-1}	r^b
VIa	maleic anhydride	9.8×10^8	c	c	
VIa	dimethyl fumarate	1.7×10^8	6.94	-1.65^d	0.979
VIa	diethyl fumarate	1.6×10^8	6.66	−2.04	0.991
VIa	fumaronitrile	5.7×10^7	7.47	−0.37	0.955
VIb	fumaronitrile	1.5×10^7			
VIa	diethyl maleate	1.9×10^6	6.28	0.0	0.999
VIa	2,3-dimethyl-2-butene	1.3×10^5			

[a] In the parent nitrile as solvent, k given at 293 K. [b] Linear correlation coefficient of Arrhenius plot. [c] Nonlinear, obeys approximately the expression $\log k = [(6.13 + 1.6) \times 10^3/T] - (2.24 \times 10^5/T^2)$. [d] Approximately nonlinear; obeys $\log k = [(4.42 + 1.79) \times 10^3/T] - (1.99 \times 10^5/T^2)$.

fluorenylidene with ketones clearly parallels the case of nitriles. Ketones lead to strong ylide signals (XXV) in the 600–650-nm region, a limited yield of 9-fluorenyl, which is considerably reduced in deuterio derivatives, and low ylide yields (or negligible) when the ketone has aromatic rings.



XXV

Reactions of Nitrile Ylides. Reactions of ylides formed by reaction of fluorenylidene with nitriles, such as acetonitrile, can be readily examined by laser flash techniques. Much of the original data attributed to triplet fluorenylidene by Schuster[16] and ourselves[18,22] should be revised since the rates measured correspond to reactions of the ylide, not the carbene.

The nitrile ylide VIa can be readily quenched by electron-deficient olefins, such as dimethyl fumarate. The result is in line with the expected reactivity of these ylides, as well as with observations in the case of other carbene-derived ylides.[23,36b] Table IV summarizes the observed reactivity for a number of olefins. The Arrhenius plots are frequently nonlinear and/or lead to negative activation energies. This is clear evidence that the reaction of nitrile ylides with olefins involves several elementary steps, at least one of which must be reversible. Our data does not indicate whether this reversible or equilibrium step precedes the interaction with the olefin; however, the data for maleic anhydride somewhat favors a mechanism where the reaction is triggered by interaction of the ylide with the olefin, with the reversible step following this interaction. This conclusion is based on the observation that the segment of the curve with negative slope tends to approach the rates and temperature dependence for diffusion control in this solvent. The detailed nature of the processes involved is as yet unknown, though it would seem that similar situations leading to negative activation energies are not uncommon in carbene chemistry.[13,16]

Mechanistic Considerations

The sensitivity of laser flash photolysis techniques to the various processes that can take place in any chemical system is roughly proportional to the product of the quantum yield of formation for any given species times its extinction coefficient. Thus, in a system where fluorenylidene in its different electronic states competes for abstraction or insertion reactions at a C–H bond, the technique will be quite sensitive to abstraction while insertion would be expected to be undetectable, as long as the products of reaction are produced in their ground states. The observed rate of triplet carbene decay or fluorenyl radical formation is the total rate of all triplet carbene processes, of which H atom abstraction is one component. The laser flash experiments cannot gauge the relative contribution of hydrogen atom transfer to the total triplet reaction. If the singlet–triplet splitting in fluorenylidene is small and spin equilibration is rapid, the rate of triplet decay may be predominantly controlled through the equilibrium singlet population.

If singlet and triplet carbene remain in equilibrium at all times, then the observed rates of quenching can be expressed as:

$$k_q = k_T + k_S K_{eq} \tag{2}$$

Again, we emphasize that this equation is valid regardless of whether the signal-generating reaction takes place from the singlet or triplet state. In the case of cyclohexane, where, as mentioned before, at most 14% of the reaction products arise from the triplet reaction, we can establish that

$$\sim 7k_T \leqslant k_S K_{eq}$$

Thus, since $k_q = 8.3 \times 10^7\ M^{-1}\ s^{-1}$ (vide supra) and if the equality holds, we would have $k_S K_{eq} \sim 7 \times 10^7\ M^{-1}\ s^{-1}$. If we assume that k_S cannot exceed diffusion control, then $K_{eq} \leqslant 0.01$, which roughly puts an upper limit of 2 kcal mol^{-1} for the energy gap. Similar arguments can be and have been applied to the methanol quenching data and lead to similar conclusions.[30] However, we are reluctant to apply a similar analysis to the data in Table II since in the case of diphenylcarbene this type of analysis has been shown to be inadequate for the prediction of T–S energy gaps.[10]

Application of a similar criteria to the data for *cis*-4-methyl-2-pentene in hexafluorobenzene leads to

$$k_q = 2.1 \times 10^8\ M^{-1}\ s^{-1} = k_T + k_S K_{eq}$$

This equation is valid only because the value of k_q was measured at low olefin concentrations where we are not likely to disrupt singlet–triplet equilibration. The very nonstereospecific nature of the cyclopropanation under these conditions[25] suggests that k_T accounts for at least 50% of the contribution to k_q: thus, $k_T \geqslant 10^8\ M^{-1}\ s^{-1}$. Since there is clear indication[25] that the equilibration can be disrupted at high olefin concentration (which required $k_T[\text{olefin}] \geqslant k_{TS}$), we believe that the value of the triplet-to-singlet interconversion, k_{TS}, cannot exceed $5 \times 10^8\ s^{-1}$, which puts an upper limit of $5 \times 10^{10}\ s^{-1}$ for k_{ST}, which compares well with Schuster's recent measurement.[21] Despite the considerable change in solvent in these experiments, the changes in polarity are not large, since the cosolvents (hexafluorobenzene and olefin) are both quite nonpolar. In addition, we observe substantial changes in product ratios when the solvent is changed from 72 to 52 mol % hexafluorobenzene (see Experimental Section), which is not as drastic a change as the overall concentration range may suggest. Results recently reported by Schuster et al.[21] suggest that solvent polarity changes (such as acetonitrile vs. cyclohexane) could induce changes in the interconversion rates.

Conclusions

Roughly 20 years have elapsed since Jones and Rettig[25] reported the first mechanistic studies of fluorenylidene. Using only product analyses these workers obtained the basic qualitative mechanistic picture. Laser flash photolysis work on fluorenylidene originally confused the area and, when clarified, merely verified the mechanistic picture developed earlier. Laser flash photolysis has led to the clear-cut identification of ylides derived from carbenes. It is true that the chemistry of many of these ylides has been well developed using other precursors. However, the contribution of laser flash photolysis has been to give a measure of the rate of ylide formation from carbenes and the absolute rate constants of ylide reactions. Laser flash photolysis also gives information on the absolute rates of reaction of fluorenylidene with different functional groups. The interpretation of the kinetic data suffers from similar limitations as does product analysis. There are two closely spaced spin states of the carbene, each of which can undergo reaction. Modern laser flash photolysis studies are much less time consuming than traditional product studies. We may then predict that laser experiments may frequently precede product work and will probably identify interesting areas in which chemical analysis will be useful and indispensable to support mechanistic hypothesis. However, we see little likelihood that laser flash photolysis or any other direct kinetic method, will supplant or replace product studies as the primary basis of understanding chemical reactions.

Experimental Section

Materials. Diazofluorene was prepared by a literature procedure.[46] All solvents were purified by the same techniques as in earlier reports.[19]

Product Studies. Reaction of Fluorenylidene with Cyclohexane. DAF, 50 mg, was dissolved in spectrograde cyclohexane to a 3×10^{-4} M solution. The sample was deoxygenated by nitrogen purging and was irradiated with visible light for 3 h at 8–10 °C. Column chromatography on silica gel eluting first with hexane and then with ether/hexane (5/95, v/v) gave 18.6 mg, 28.8%, of **XVI**, which was identified by GC/mass spectroscopy: *m/e* 164 (100%), 248 (p^+). In addition, fluorene ketazine (23.4 mg, 50.5%) was isolated and was identified by comparison with an authentic sample.[47] The yields of these products were based on starting DAF.

Photolysis of a 1×10^{-3} M solution of DAF in cyclohexane and analysis by gas chromatography gave the following relative yields of volatile products (uncorrected for relative response factors): bicyclohexyl (XV, 0.13%), fluorene (7.8%), (9-fluorenyl)cyclohexane (XVI, 65.4%), 9,9′-bifluorenyl (XVII, 9.4%). At high DAF concentrations ($\geq$0.01 M) the relative yields of XVII increase, presumably as a result of other (probably nonradical) processes.

Reaction of Fluorenylidene with Acetonitrile. DAF (200 mg) was dissolved in acetonitrile (1 L) that had been carefully dried by distillation from calcium hydride. The solution was kept screened from light and was deoxygenated by nitrogen purging. It was then photolyzed ($\lambda > 316$ nm), which caused the pink solution to turn brown. This color change effectively screened the DAF from further photolysis and prevented the determination of yields on the basis of DAF consumed because the unreacted diazo compound could not be cleanly separated from other products (vide infra).

The acetonitrile was removed by rotary evaporation, and the crude product was analyzed by GC/mass spectroscopy using a 6 ft, 6% OV-101 column. Some unreacted DAF was present. Four other products were detected all of which contained acetonitrile moieties. Two isomers that were poorly separated on the GC column were assigned as XIX (~25%) and XX (~25%) on the basis of their mass spectrum (*m/e* (relative abundance) XIX, 205 (23.2), 178 (9.1), 165 (100.0); XX, 205 (33.2), 190 (12.5), 164 (100.0)). A third product (~25%) contained two acetonitrile moieties (*m/e* (relative abundance) 244 (30.2), 229 (17.4), 203 (100.0), 163 (16.8)). The final product (~25%) appeared to be an oxide of XX (*m/e* (relative abundance) 221 (41.9), 206 (48.1), 179 (100.0), 165 (13.2)), which may have been formed from residual oxygen remaining in the reaction mixture.

Several attempts were made to identify all of the reaction products. Column or thin-layer chromatography on silica gel using a variety of solvents did not lead to clean separations of the highly colored and involatile products which had poor solubility in organic solvents. Indeed we were only successful on enriching one of the fractions in XIX. It seems that product studies including yields based on starting materials are only practical on such dilute solutions when photolysis leads to products that are more weakly absorbing than the starting materials.

Reaction of Fluorenylidene with *cis*-4-Methyl-2-pentene in Hexafluorobenzene. Two experiments were carried out on the photodecomposition of DAF in mixtures of *cis*-4-methyl-2-pentene (XXI) and hexafluorobenzene so as to confirm the data reported in earlier publications.

In a typical experiment hexafluorobenzene (7.0 mL), which had been distilled from potassium carbonate, was mixed with the olefin (3.0 mL). DAF (14 mg) was added to the mixture, and the solution was deoxygenated by nitrogen purging. The sample was then photolyzed (350 nm) until the pink color was discharged. Control experiments showed that prolonged photolysis did not change the product distribution. The samples were concentrated by rotary evaporation and were analyzed by GC/mass spectroscopy. The products were assigned by using compounds XXII and XXIII as standards. These were supplied by Professor M. Jones, Jr., and had the appropriate NMR and mass spectra.

At hexafluorobenzene concentrations of 72 and 52 mol % the, respective ratios of XXII/XXIII were 0.29 and 0.43, in good agreement with published results.[25] In addition to XXII and XXIII a small quantity (ca. 20% based on the combined yields of XXII and XXIII) of the fluorenylidene adduct to hexafluorobenzene was also detected (*m/e* 350 (M^+), 192 (100%), XXIV). The same product was detected when DAF was photolyzed in hexafluorobenzene as well as fluorene ketazine. Under conditions of poor GC resolution the hexafluorobenzene adduct had the same retention time as XXII; however, such contributions serve only to enhance the ratio of XXII/XXIII and do not effect the conclusions of earlier work.

Laser Flash Photolysis. These experiments were carried out in deaerated samples contained in Suprasil tubes made of rectangular (7×3 mm^2) tubing. Most measurements were carried out in static samples (1 or 2 mL); however, a flow system was preferred for the recording of transient spectra.

The pulses from a Molectron-UV-24 nitrogen laser (337.1 nm, ~8 ns, up to 10 mJ) were used for excitation. The signals, initially captured by a Tektronix R7912 transient digitizer, were then transferred to a PDP-11/23 computer, which also controlled the experiment and provided suitable processing, storage, and hardcopy facilities. Further details can be found elsewhere.[48]

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Registry No. I, 832-80-4; VIa, 83693-17-8; VIb, 88413-57-4; XIII, 2299-68-5; XV, 92-51-3; XVI, 32501-56-7; XVII, 1530-12-7; XVIII, 2071-44-5; XIX, 21745-43-7; XX, 16504-40-8; XX (oxide), 88413-53-0; XXI, 691-38-3; XXII, 88413-54-1; XXIII, 88413-55-2; XIV, 88413-56-3; CH_3CN, 75-05-8; C_6F_6, 392-56-3; CH_3OH, 67-56-1; CH_3COOH, 64-19-7; CH_3OD, 4206-31-9; fluorenylidene, 2762-16-5; cyclohexane, 110-82-7; fluorene, 86-73-7; 2-methyl-2-pentene, 625-27-4; 2,3-dimethylbut-2-ene, 563-79-1; diethyl fumarate, 623-91-6; maleic anhydride, 108-31-6; dimethyl fumarate, 624-49-7; fumaronitrile, 764-42-1; diethyl maleate, 141-05-9; hydrogen, 1333-74-0.

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