systems where one or more pertinent features (e.g., spectral, structure, ligand type required, redox behavior expected, etc.) can be examined in detail, one strives to elucidate those factors contributing to the observed unique characteristics possessed by the natural system. From this point of view, it may be expected that the model approach will yield certain kinds of information unavailable directly from studies of the proteins.[1]

Further chemical investigations of I–IV and their analogues are in progress, in order to identify Cu–O_2 intermediates and elucidate those structural and electronic factors required for this copper ion mediated oxygenation.

Acknowledgment. We thank Research Corporation (KDK) and the National Institutes of Health (KDK GM 28962; JZ GM 22566 and GM 27459) for support of this research. We also thank Dr. C. E. Costello for field-desorption mass spectrometric analyses carried out at the MIT Mass Spectrometry Facility (supported in part by NIH RR00317; P. I.: Professor K. Biemann), and Dr. J. R. Hyde for assistance in collection of X-ray data.

Registry No. I, 79854-06-1; II, 82731-39-3; IIIB, 86593-51-3; IV, 89017-39-0; $Cu(CH_3CN)_4PF_6$, 64443-05-6; α,α'-dibromo-*m*-xylene, 626-15-3; bis(2-(2-pyridyl)ethyl)amine, 15496-36-3; diisopropylethylamine, 7087-68-5; 2-vinylpyridine, 100-69-6; *m*-xylylenediamine, 1477-55-0; oxygen, 7782-44-7; monooxygenase, 9038-14-6.

Supplementary Material Available: Listings of structure factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for compounds II (Tables VI–X) and IIIB (Tables XI–XV) (48 pages). Ordering information is given on any current masthead page.

Addition of Fluorenylidene to 1,2-Dichloroethylenes. Effects of Additives and the Question of Spin-State Equilibrium[†]

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Abstract: The photolysis of diazofluorene in *cis*- and *trans*-1,2-dichloroethylene has been studied. While cyclopropanation of the trans isomer is >92% stereospecific, the stereoselectivity of addition to the cis isomer is less than 86%. In the presence of styrene or butadiene the degree of stereoselectivity increases, and both the absolute and relative yields of an adduct formed via rearrangement of a diradical intermediate, 9-(2,2-dichloroethylidene)fluorene, decrease. An opposite trend both in stereoselectivity and yield of rearrangement product is observed when reaction mixtures are diluted with hexafluorobenzene. Other diluents, trichlorotrifluoroethane, perfluoromethylcyclohexane, tetramethylsilane, and benzene, have little effect on the stereoselectivity of cyclopropanation. In the presence of the highly reactive substrate methanol, the stereoselectivity of cyclopropane formation from *cis*-1,2-dichloroethylene is also unperturbed. It is suggested that both singlet and triplet fluorenylidene are present as reactive intermediates, singlet reacting with dichloroethylene exclusively by stereospecific cis addition and triplet fluorenylidene yielding stereoisomeric cyclopropanes and rearrangement product via a diradical adduct. Interconversion of these carbene spin states seems to be rapid compared to their reactions with dichloroethylene and methanol, but not so rapid as the reactions of triplet fluorenylidene with styrene and butadiene. The effect of hexafluorobenzene may be to form a carbenoid that can mimic triplet fluorenylidene.

The addition of carbenes to olefins yielding cyclopropanes is a reaction both preparatively and mechanistically useful.[1] Traditionally the stereospecificity of cyclopropane formation has been the most frequently employed means to distinguish the spin states of reacting carbenes.[2] Quantitative assay of the ratio of singlet and triplet carbenes undergoing reaction has been difficult, however, because the ratio of stereoisomeric cyclopropanes formed from the triplet carbene is generally not known.[3] This problem does not exist for a reagent that gives quite different products from singlet and triplet carbenes.[4]

It has been reported that the 1,2-dichloroethylenes react to give products of different structure from the lowest singlet and triplet states of carbenes.[5–7] Singlet $:CBr_2$,[5] $:CCl_2$,[5] $:C(CO_2CH_3)_2$,[6] and $:C(C_6H_5)_2$[7] undergo addition to the *cis*-olefin with a high degree of stereospecificity (>90%) to yield *cis*-1,2-dichlorocyclopropanes, while triplet $:C(CO_2CH_3)_2$[6] and $:C(C_6H_5)_2$[7] give products of addition with rearrangement, $R_2C{=}CHCHCl_2$ (see Scheme I). That an organometallic carbenoid formed from $:CBr_2$ also gives a product of addition with rearrangement[8] injects a note of caution but does not lessen the utility of the 1,2-dihaloethylenes as reagents for mechanistic studies of carbenes, and their use has enabled us to present new evidence for the establishment of a mobile singlet–triplet equilibrium in the reactions of diphenylmethylene.[7]

The key step that avoids the formation of cyclopropanes from the reactions of previously studied triplet carbenes with 1,2-dichloroethylenes is believed to be a rearrangement by chlorine atom migration of diradical intermediate I in Scheme I. It is assumed that spin is conserved in the initial carbene additions, and therefore thermochemistry dictates that intersystem crossing must precede ring closure of I. Intersystem crossing must also then be a discrete step in the rearrangement sequence, but may occur after chlorine migration.

[†] This work has been supported by the National Science Foundation under Research Grants CHE-75-20163 and CHE-80-19638.

(1) W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press, New York, 1971.

(2) P. P. Gaspar and G. S. Hammond, "Spin States in Carbene Chemistry", Vol. II, R. A. Moss and M. Jones, Jr., Eds., Wiley-Interscience, New York, 1975, pp 207–362.

(3) Our discussion assumes that the lowest singlet and triplet states of the reacting carbene are responsible for the bulk of the products. This may not always be the case and there are several reports of the reactions of higher excited states: K. T. Chang and H. Shechter, *J. Am. Chem. Soc.*, **101**, 5082 (1979); G. R. Chambers and M. Jones, Jr., *ibid.*, **102**, 4516 (1980).

(4) The first such reagent was 1,1-dicyclopropylethylene: N. Shimizu and S. Nishida, *J. Am. Chem. Soc.*, **96**, 6451 (1974).

(5) J. B. Lambert, K. Kobayashi, and P. H. Mueller, *Tetrahedron Lett.*, 4253 (1978).

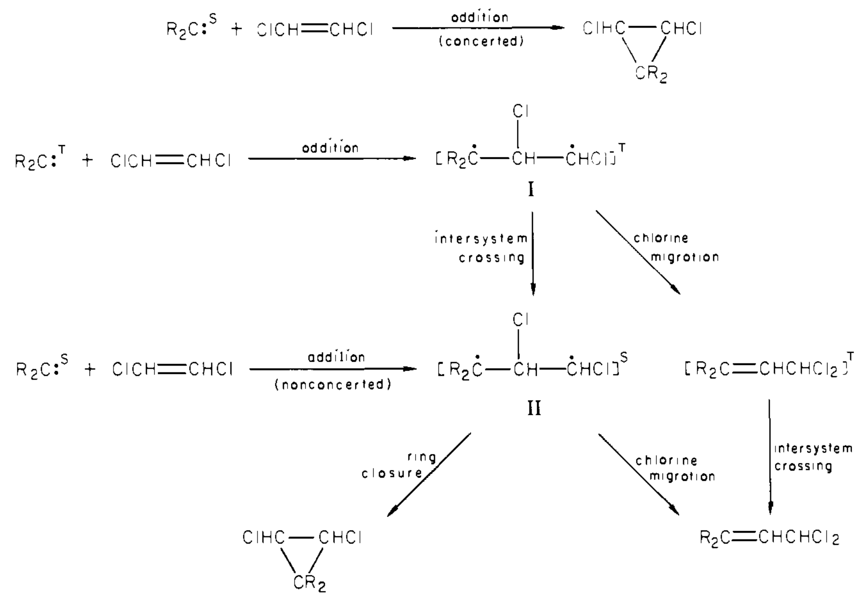
(6) M. Jones, Jr., V. J. Tortorelli, P. P. Gaspar, and J. B. Lambert, *Tetrahedron Lett.*, 4257 (1978).

(7) P. P. Gaspar, B. L. Whitsel, M. Jones, Jr., and J. B. Lambert, *J. Am. Chem. Soc.*, **102**, 6108 (1980).

(8) J. B. Lambert, P. H. Mueller, and P. P. Gaspar, *J. Am. Chem. Soc.*, **102**, 6615 (1980).

0002-7863/84/1506-2128$01.50/0

Scheme I



That very little cyclopropane is formed from triplet dicarbomethoxy- and diphenylmethylene may be due to the rapidity of chlorine migration relative to intersystem crossing for the triplet diradical adduct I, but the predominance of rearrangement in the addition of triplet carbene may result from a chlorine shift that is more rapid than ring closure of the singlet diradical II.

There is certainly no reason to believe that rearrangement of I will be more rapid than eventual ring closure for all carbenes.[7] Indeed ring closure is more rapid than rearrangement when 1,1-dicyclopropylethylene is employed as a carbene-trapping agent, and ring opening of the resulting cyclopropylcarbinyl radical moiety is possible.[4]

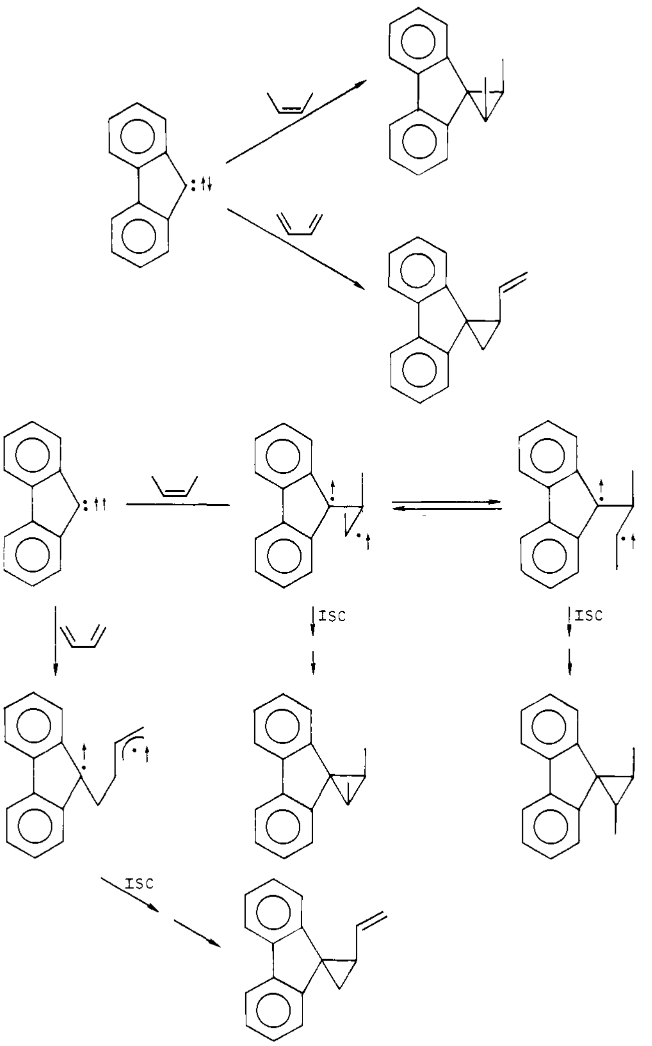
It is generally believed[5-7] that singlet carbenes react with 1,2-dihaloethylenes via a concerted cis addition according to the Skell postulate.[9] We have argued that singlet carbenes need not undergo concerted addition, but that conformational equilibration in a diradical is likely to be more rapid than ring closure.[10] A singlet carbene could also give rise to rearrangement product if both nonconcerted addition and rapid chlorine migration occurred (Scheme I). The stereospecific formation of cyclopropanes from *cis*-1,2-dichloroethylene implies that the cyclopropane comes predominantly from a singlet carbene.

Fluorenylidene, while long considered a "normal carbene"[11] in the sense of undergoing efficient cyclopropanation and displaying reactions of discrete singlet and triplet electronic states, has recently had a number of unusual properties attributed to it. It was therefore hoped that study of the reactions of fluorenylidene with dichloroethylenes might shed new light both on the chemistry of fluorenylidene and on the use of 1,2-dihaloethylenes as spin-state monitors in carbene chemistry.

The remainder of this introduction briefly reviews the varied and sometimes conflicting interpretations of fluorenylidene chemistry.

In 1965 Jones and Rettig found that the addition of fluorenylidene to *cis*-2-butene was not stereospecific and that the ratio of *cis*- to *trans*-cyclopropane products decreased when hexafluorobenzene was present in the reaction mixture and increased in the presence of 1,3-butadiene.[12] It was concluded that two reaction intermediates were formed, one of which underwent stereospecific addition to olefins and could relax to the other. The former was considered to be the singlet carbene, while the species that added nonstereospecifically and was much more reactive toward butadiene than toward monoolefins was believed to be the triplet carbene. Variation of the product ratios with the composition of the reaction mixture was attributed to rates of reaction

Scheme II



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[9] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

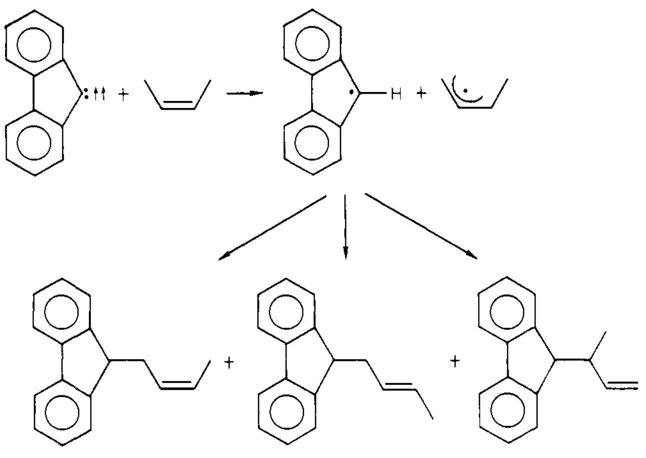
[10] P. P. Gaspar and G. S. Hammond, "The Spin States of Carbenes" (Carbene Chemistry), 1st ed., W. Kirmse, Ed., Academic Press, New York, 1964, pp 235–274.

[11] W. J. Baron, M. R. De Camp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn, "Carbenes", Vol. I, M. Jones, Jr., and R. A. Moss, Eds., Wiley-Interscience, New York, 1973, p 79.

[12] M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4013, 4015 (1965).

for both singlet and triplet fluorenylidene more rapid than their rates of interconversion.

Moss and Joyce studied the variation of product yields from fluorenylidene and various butene isomers over a wide temperature range, from solution experiments at 0 °C down to solid mixtures at −196 °C.[13] The yield of cyclopropanes decreased dramatically in the solid phase, but the cyclopropane stereoisomer ratio from *cis*-2-butene changed very little. There was a large increase at low temperature in the yields of products attributed to allylic hydrogen abstraction by triplet fluorenylidene followed by geminate recombination.[13]



Moss and Joyce suggested that photolysis of diazofluorene produces a roughly equal mixture of singlet and triplet carbenes and that singlet can either add stereospecifically or relax to the triplet. If the activation energy for addition of triplet fluorenylidene is larger than that for hydrogen abstraction, while the preexponential factors favor addition, then as the temperature is lowered abstraction will gain on addition for the triplet carbene.[13] The rates of interconversion of the carbene spin states were assumed to be slower at all temperatures than their reaction rates.

The study of fluorenylidene by kinetic spectroscopy led to reports of particularly unusual chemical properties.

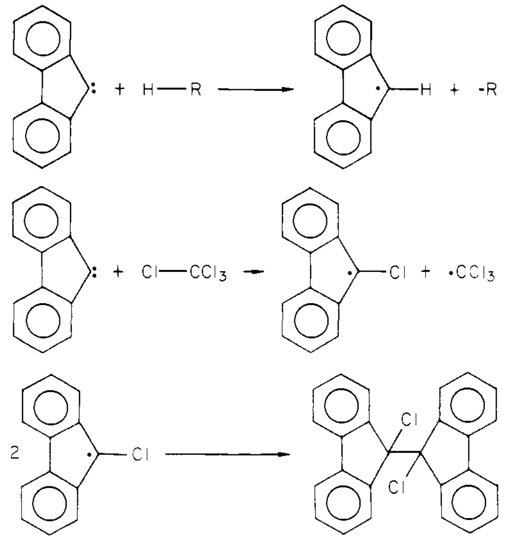
In 1980 Zupancic and Schuster reported the detection of two short-lived intermediates in the nanosecond time-scale laser photolysis of diazofluorene in acetonitrile solution at room temperature.[14] The shorter-lived transient, $t_{1/2} = 17 \pm 2$ ns, λ_{max} 470 nm, was believed to be singlet fluorenylidene, while absorption maxima at 400 and 500 nm whose rate of growth was equal to the rate of decay of the absorption at 470 nm were assigned to triplet fluorenylidene.[15] These assignments were supported by quenching experiments with methanol, believed to be a selective trapping agent for singlet carbenes.[16] In the presence of methanol the transients assigned to triplet fluorenylidene were smaller, and a high yield of 9-methoxyfluorene was isolated. The following rate constants were deduced for reaction with the 470-nm transient: monoolefins, 2 to 9×10^8 M^{-1} s^{-1}; *trans*-piperylene, 1.03×10^9 M^{-1} s^{-1}; methanol, 8.45×10^8 M^{-1} s^{-1}; and *tert*-butyl alcohol, 1.51×10^8 M^{-1} s^{-1}.

The temperature dependence of the disappearance of the transient with λ_{max} 470 nm, assigned to singlet fluorenylidene by Zupancic and Schuster, was also measured.[17] In pure acetonitrile the process responsible for the disappearance of the 470-nm transient had activation parameters of $\Delta H^{\ddagger} = 1.99 \pm 0.05$ kcal mol^{-1} and $\Delta S^{\ddagger} = -17.0 \pm 2.0$ eu and was believed to be intersystem crossing. In the presence of olefins the 470-nm transient was consumed by processes whose activation enthalpies were small, and some negative. The largest was -1.2 ± 0.5 kcal mol^{-1} for methyl methacrylate. The activation entropies were all near −20 eu, similar to that imputed to intersystem crossing!

A combination of rate measurements utilizing laser flash techniques and product studies led Schuster and co-workers to the fascinating but erroneous suggestion that singlet fluorenylidene undergoes nonstereospecific addition to olefins.[18] By measuring the rate constants for disappearance of the 470-nm transient in acetonitrile solutions containing *cis*- or *trans*-β-methylstyrene, or *cis*-2-pentene (2 M), it was demonstrated that greater than 90% of the carrier, believed to be singlet fluorenylidene, was consumed by reaction with the olefins rather than by conversion to the 400- and 500-nm transients associated with triplet fluorenylidene. Analysis of the stable reaction products revealed that more *trans*- than *cis*-cyclopropanes were formed from the *cis*-olefins. Attribution of nonstereospecific addition to singlet fluorenylidene was bolstered by the agreement found in comparisons of product ratios from experiments in which the singlet carbene trap methanol was allowed to compete with olefin, and product ratios derived from measured rate constants for the disappearance of the 470-nm transient.

No special role was assigned to the acetonitrile solvent because the rate constant for disappearance of the 470-nm transient in the presence of olefin was found to be nearly the same in Freon 113 as in acetonitrile solution.[18] When laser photolysis of diazofluorene was carried out in pentane or cyclohexane, however, the only transient observed was at 497 nm with a half-life of 3 μs, and it was assigned to the fluorenyl radical.[14]

Formation of fluorenyl radicals by hydrogen and halogen atom abstraction was ascribed to singlet fluorenylidene by Wong, Griller, and Scaiano on the basis of a reattribution of the 500-nm transient observed by Schuster to the fluorenyl radical.[19] Since both the 500-nm transient and the 400-nm transient assigned by Schuster to triplet fluorenylidene grew at the same rate that the 470-nm transient underwent decay, *singlet* fluorenylidene was believed responsible for hydrogen abstraction. 9-Fluorenyl radical formation by abstraction from cyclohexane in excess acetonitrile was found to occur with a rate constant of 8.3×10^7 M^{-1} s^{-1} at 30 °C compared with ca. 2.9×10^7 M^{-1} s^{-1} for abstraction from acetonitrile.[20] The appearance of a new transient with λ_{max} 490 nm when diazofluorene was irradiated in carbon tetrachloride was attributed to the formation of the 9-chlorofluorenyl radical whose dimer was isolated in ca. 50% yield.



Recently the assignments of the 400- and 470-nm transients have also been revised.[21,22] The 400-nm transient previously

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[13] R. A. Moss and M. A. Joyce, *J. Am. Chem. Soc.*, **100**, 4475 (1978).

[14] J. J. Zupancic and G. B. Schuster, *J. Am. Chem. Soc.*, **102**, 5958 (1980).

[15] The assumption that the 400- and 500-nm absorptions were due to a single transient species was not justified. If A reacts to give B and C (e.g., A → B + C) then B and C are formed with the same lifetime as A decays.

[16] W. Kirmse, K. Loosen, and H.-D. Sluma *J. Am. Chem. Soc.*, **103**, 5935 (1981), and earlier references contained therein.

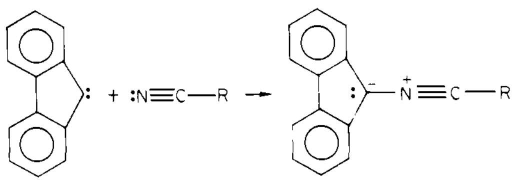
[17] J. J. Zupancic and G. B. Schuster, *J. Am. Chem. Soc.*, **103**, 944 (1981).

[18] J. J. Zupancic, P. B. Grasse, and G. B. Schuster, *J. Am. Chem. Soc.*, **103**, 2423 (1981).

[19] P. C. Wong, D. Griller, and J. C. Scaiano, *J. Am. Chem. Soc.*, **103**, 5934 (1981).

[20] Estimated by use of eq 1, ref 19.

associated with triplet fluorenylidene[16-19,23] was detected only in nitrile solvents and therefore reassigned to a nitrile ylid:[24]



The enhanced lifetime of the 470-nm transient in hexafluorobenzene (95 ns vs. 27 ns in acetonitrile) and its rapid disappearance when an olefin, *cis*-4-methyl-2-pentene, was present in the hexafluorobenzene solution were both explained by its reassignment to triplet fluorenylidene.[21] The rate constant for quenching of the 470-nm transient by *cis*-4-methyl-2-pentene in hexafluorobenzene, 2.1×10^8 M^{-1} s^{-1}, was sufficiently large that even at 5 mol %, the olefin would consume more than 90% of the transient. Therefore, the variation in product ratio with hexafluorobenzene concentration observed by Jones and Rettig[12] would not be expected if the 470-nm transient had been due to singlet fluorenylidene. Griller et al. attributed their failure to observe singlet fluorenylidene to a lifetime less than 10 ns, the time resolution of their laser.[21]

Since most ylides have singlet ground states, it was speculated that triplet fluorenylidene might be converted to an ylide on reaction with a nitrile via singlet fluorenylidene in rapid equilibrium with the triplet, with an equilibrium constant

$$S \overset{K}{\rightleftharpoons} T$$

greater than ten and addition to olefins competitive with intersystem crossing.[21]

Schuster and co-workers have recently reported results from picosecond laser spectroscopy as well as low-temperature matrix isolation experiments.[22] They found that the first transient observed in the picosecond scale photolysis of diazofluorene, with λ_{max} 470 nm, is not detectable at 100 ps after irradiation, but grows in with a half-time of 0.28 ± 0.90 ns. There is therefore an unobserved precursor, presumed to be singlet fluorenylidene, of the 470-nm transient now believed to be due to triplet fluorenylidene.

In cyclohexane and spiropentane the 470-nm transient is observed, and its decay is accompanied by growth, at the same rate, of the 500-nm transient attributed to the 9-fluorenyl radical. The half-times are 1.4 ± 0.6 ns in cyclohexane and 29 ± 6 ns in spiropentane. In 2-methyltetrahydrofuran glass at 10 K irradiation of diazofluorene gives a species stable at that temperature that absorbs with λ_{max} 470 (major) and 442 (minor) nm. The ESR spectrum of triplet fluorenylidene is observed at the same temperature on a different sample.

The apparently rapid reaction of *triplet* fluorenylidene with alcohols yielding fluorenyl ethers prompted Schuster to suggest that equilibrium was rapidly established between singlet and triplet fluorenylidene.[22] When diazofluorene was irradiated in spiropentane the initial concentration of the 470-nm transient that can now be safely called triplet fluorenylidene was not affected by the presence of ethanol, but the rate of decay of the transient and that of the growth of the 500-nm transient, believed to be fluorenyl radical, both increased. The *amount* of fluorenyl radical formed, however, decreased. A rate constant for the *apparent* reaction of triplet fluorenylidene and ethanol of $2.0 \pm 0.4 \times 10^8$ M^{-1} s^{-1} was deduced. When a triplet sensitizer xanthone was present during the irradiation of diazofluorene in methanol-containing acetonitrile solutions, 9-methoxyfluorene was the major product, formed in 92% yield, but the formation of the ether was slowed by a factor of 40 in the presence of a triplet quencher, 2,5-dimethyl-2,4-hexadiene. Since ether formation is attributed to *singlet* carbenes,[16] Schuster suggested that singlet and triplet fluorenylidene were in equilibrium, with the reaction of the singlet with alcohol being slower than singlet–triplet interconversion.[22]

The ether-to-cyclopropane product ratios from photolysis of diazofluorene in mixtures of methanol and various olefins reported earlier by Schuster agreed closely with ratios derived from the rate constants for the disappearance of the 470-nm transient now seemingly established as triplet fluorenylidene. The conclusion seems unavoidable that *either* all observed products come directly from the 470-nm transient, *or* the selectivity of all product-forming intermediates is the same, *or* intermediates of different selectivity, such as singlet and triplet fluorenylidene, are in mobile equilibrium.

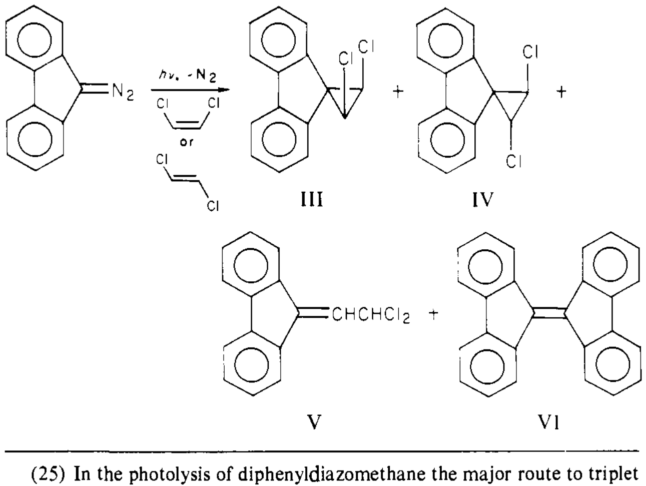
Thus the recent experiments have challenged the view, based on the work of Jones and Rettig,[12] that the relaxation of singlet fluorenylidene to the triplet ground state is slow compared to its rate of reaction with olefins and therefore that the singlet and triplet carbenes were not in equilibrium.

Schuster's observation that the 470-nm transient is not observed 100 ps after the flash photolysis of diazofluorene in acetonitrile suggests further that triplet fluorenylidene is formed exclusively from relatively long-lived precursors such as singlet fluoreneylidene.[25,26] This is compatible with the nonstereospecific cyclopropanation observed by Jones and Rettig[12] if singlet-to-triplet intersystem crossing can compete with reaction of the singlet carbene with olefin. The changes in product ratios with concentration of added hexafluorobenzene and butadiene point, however, to comparable rates of intersystem crossing and reaction (Scheme III).

Results and Discussion

Reaction of Fluorenylidene with *cis*- and *trans*-1,2-Dichloroethylene. Previous experiments had indicated that singlet carbenes react with the 1,2-dichloroethylenes predominantly by stereospecific addition and triplet carbenes by addition with rearrangement.[5-7] Fluorenylidene was therefore generated in the presence of *cis*- and *trans*-1,2-dichloroethylene in the hope that the products would allow inferences to be made concerning the proportions of singlet and triplet carbene undergoing reaction.

When dilute (0.05 M) degassed solutions of diazofluorene in *cis*- and *trans*-1,2-dichloroethylene were irradiated with a medium pressure mercury lamp filtered with uranium glass, four products were formed: *cis*- and *trans*-2,3-dichlorospiro[cyclopropane-1,9′-fluorene] (hereafter designated cyclopropanes III and IV, respectively), 9-(2,2-dichloroethylidene)fluorene (rearrangement product V), and bifluorenylidene (VI). Yields are given in Tables I and II.



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(21) D. Griller, C. R. Montgomery, J. C. Scaiano, M. S. Platz, and L. Hadel, *J. Am. Chem. Soc.*, **104**, 6813 (1982).

(22) B.-E. Brauer, P. B. Grasse, K. J. Kaufmann, and G. B. Schuster, *J. Am. Chem. Soc.*, **104**, 6814 (1982).

(23) P. C. Wong, D. Griller, and J. C. Scaiano, *Chem. Phys. Lett.*, **83**, 69 (1981).

(24) P. C. Wong, D. Griller, and J. C. Scaiano, *J. Am. Chem. Soc.*, **104**, 6631 (1982).

(25) In the photolysis of diphenyldiazomethane the major route to triplet diphenylmethylene is intersystem crossing from the singlet carbene. A minor pathway is the decay of an excited triplet diphenylmethylene: C. DePuy, G. M. Korenowski, M. McAuliffe, W. M. Hetherington, and K. B. Eisenthal, *Chem. Phys. Lett.*, **77**, 272 (1981).

(26) It is striking, however, that upon flash photolysis of diazofluorene in cyclohexane, an absorption maximum at 470 nm *was* observed at 100 ps by Schuster (see ref 22).

Scheme III

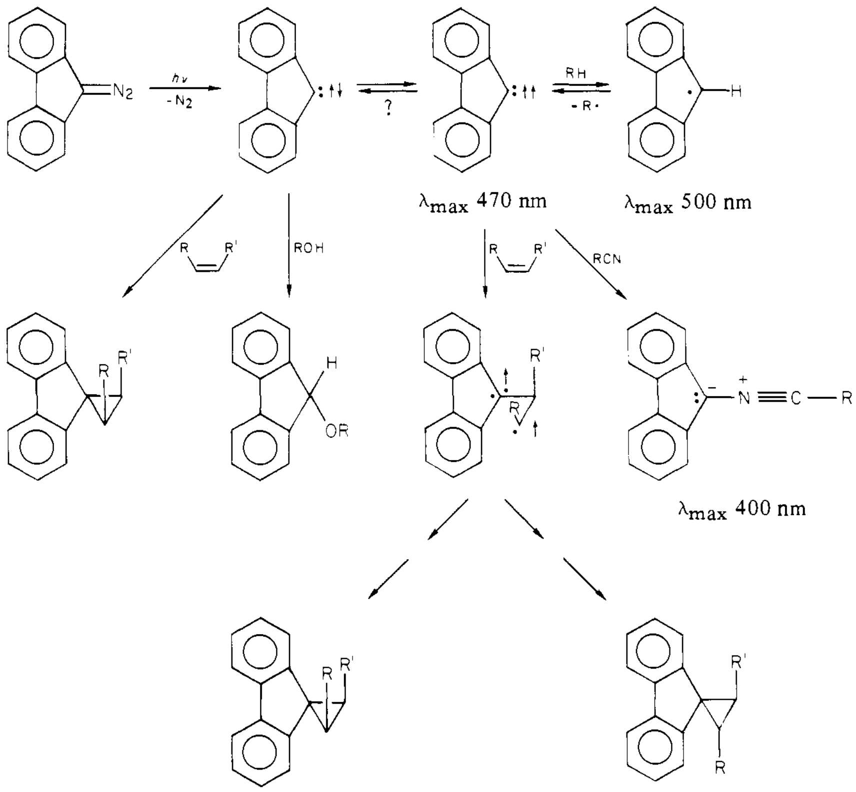
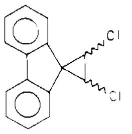
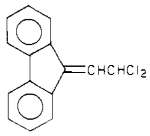
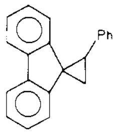
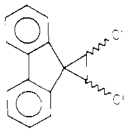
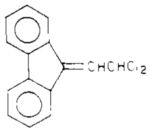
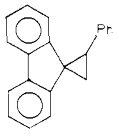


Table I. Irradiation of 9-Diazofluorene (DFL) in Mixtures of *trans*-1,2-Dichloroethylene and Styrene

reactants		product yields, % (absolute)				
mol % of styrene	initial concn of DFL, mol L^{-1}	 III + IV	 V	 VII	stereospecificity of cyclopropanation (IV)(100)/(III + IV)	(V)(100)/ (III + IV)
0[a]	0.051	33.2 ± 1.9	22 ± 4	0	92.2 ± 1.0	66 ± 13
0	0.100	33.0 ± 2.0	25 ± 5	0	93.0 ± 0.5	76 ± 16
0.25	0.070	49.9 ± 3.1	30 ± 6	6.6 ± 1.0	91.7 ± 0.4	60 ± 13
0.50	0.076	44.2 ± 2.3	24 ± 5	11.6 ± 1.6	91.3 ± 0.3	54 ± 12
1.00	0.072	30.9 ± 1.9	15 ± 3	17.7 ± 0.7	91.9 ± 0.6	49 ± 10
1.00	0.040	26.8 ± 1.3	11 ± 3	17.1 ± 1.0	94.0 ± 0.5	41 ± 11
2.00	0.068	32.3 ± 0.9	11 ± 3	39.1 ± 0.8	91.5 ± 0.5	34 ± 9
3.00	0.074	28.8 ± 2.3	10 ± 2	44.7 ± 2.8	91.1 ± 0.2	35 ± 7

[a] 8.8% absolute yield of bifluorenylidene (VI) was isolated from the reaction of DFL in the absence of styrene.

Table II. Irradiation of 9-Diazofluorene (DFL) in Mixtures of *cis*-1,2-Dichloroethylene and Styrene

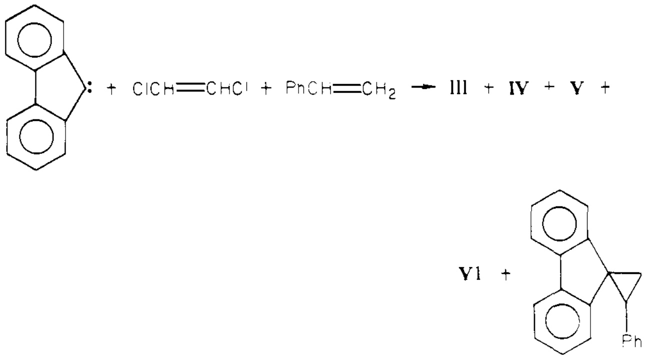
reactants		product yields, % (absolute)				
mol % of styrene	initial concn of DFL, mol L^{-1}	 III + IV	 V	 VII	stereospecificity of cyclopropanation (III)(100)/(III + IV)	(V)(100)/ (III + IV)
0	0.051	41.4 ± 1.1	10 ± 2	0	86.4 ± 0.5	24 ± 5
0	0.100	30.5 ± 2.1	12 ± 3	0	81.0 ± 0.5	39 ± 10
0.25	0.074	49.4 ± 2.9	13 ± 3	5.6 ± 0.7	87.1 ± 0.5	26 ± 6
0.50	0.052	48.1 ± 1.0	8 ± 2	13.1 ± 0.7	87.8 ± 0.3	17 ± 4
1.00	0.068	48.4 ± 2.6	10 ± 2	19.3 ± 1.1	87.4 ± 0.5	21 ± 4
1.00	0.040	30.8 ± 3.7	14 ± 3	15.4 ± 1.3	87.0 ± 0.5	45 ± 11
1.50	0.071	42.0 ± 2.3	8 ± 2	15.0 ± 1.1	89.5 ± 0.2	19 ± 5
2.00	0.071	32.3 ± 2.0	trace	29.6 ± 1.5	90.4 ± 0.4	
3.00	0.069	36.3 ± 2.2	trace	45.8 ± 2.3	91.5 ± 0.4	
5.00	0.069	25.5 ± 0.8	trace	48.5 ± 1.9	92.5 ± 0.4	

As in the case of *trans*-2-butene,[12] addition of fluorenylidene to *trans*-1,2-dichloroethylene is quite stereoselective, with greater than 90% of the cyclopropane product being the trans isomer IV. Since the *trans*-cyclopropane is likely to be more stable than the *cis*-cyclopropane, even the cyclopropane produced by cyclization of a diradical intermediate from addition of triplet carbene to the *trans*-olefin would be expected to be predominantly trans (see Scheme I). Little cyclization of the 1,3-diradical was anticipated, however, since we had previously found stereospecific cyclopropanation of 1,2-dichloroethylenes by mixtures of singlet and triplet carbenes.[6,7] This suggested that rearrangement to product V was the more likely fate of the initial adduct from triplet fluorenylidene, and indeed some V is formed, albeit in low yield.

It was therefore surprising that addition of fluorenylidene to *cis*-2-dichloroethylene is *not* stereospecific, the cis-isomer III comprising only 81 to 86% of the cyclopropane products. Since this addition is, however, considerably more stereoselective than that observed with *cis*-2-butene (the *cis*-:*trans*-cyclopropane product ratio was 1.95, or 66% cis),[12] and the formation of product V from the rearrangement of a diradical intermediate is again observed, although in even lower yield than from *trans*-1,2-dichloroethylene, it seems clear that the diradical intermediate undergoes competitive cyclization and ring closure. While a priori the diradical adduct could be formed from either singlet or triplet carbene, the results of competition experiments reported below suggest that the diradical adduct comes almost entirely from triplet fluorenylidene, as shown in Scheme I above.

Reaction of Fluorenylidene with Mixtures of Styrene and the 1,2-Dichloroethylenes. The 1,2-dichloroethylenes, as rather electron-poor olefins equipped with heteroatom substituents, are effective reaction substrates for both singlet and triplet carbenes. Competition experiments were therefore undertaken employing reagents expected to display some selectivity between carbene spin states.

The effects of added styrene on the product yields from photodecomposition of diazofluorene in *trans*- and *cis*-1,2-dichloroethylene were next investigated. Styrene had been found to be ca. 50 times as reactive as *trans*-1,2-dichloroethylene toward singlet diphenylmethylene, and ca. 170 times as reactive toward triplet diphenylmethylene.[7] In the present experiments styrene was 50 ± 10 times as reactive as either 1,2-dichloroethylene toward the mixture of fluorenylidene spin states. 2-Phenylspiro[cyclopropane-1,9′-fluorene] (VII) is formed in addition to products III–VI (see Tables I and II).



VII

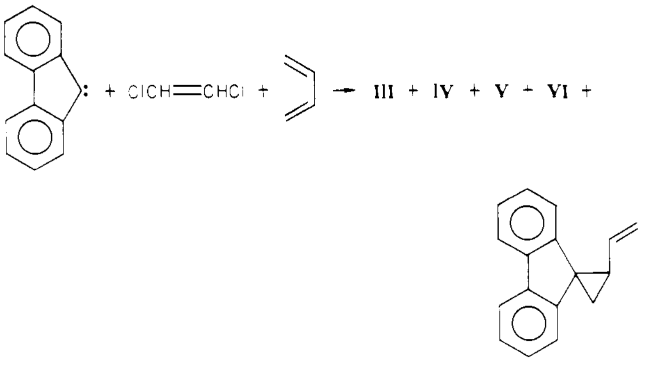
The stereospecificity of cyclopropanation of the *trans*-dichloroethylene is unaffected by the presence of styrene, but there is a slight decrease in the ratio of rearrangement product V to the cyclopropane products III + IV. This trend is more marked with *cis*-olefin, and there is a modest increase in the stereospecificity of cyclopropanation, from 86% without styrene to 92% with 0.05 mol fraction of styrene present.

These results point to the presence of at least two different species that give rise to the dichlorocyclopropane products III and IV, and suggest that only one of the reactive species undergoes addition to the *cis*-olefin with a high degree of stereospecificity. These reactive intermediates appear *not* to be in equilibrium in reaction mixtures containing as little as 2% styrene, but equilibrium may however be established in the absence of styrene, which is ca. 50 times as reactive as the dichloroethylenes toward fluorenylidene.

If it is accepted that the two species that can cyclopropanate 1,2-dichloroethylenes are singlet and triplet carbenes, then triplet fluorenylidene is the first triplet carbene to yield cyclopropanes from the 1,2-dichloroethylenes in addition to a product of addition with rearrangement. In terms of Scheme I this finding implies that intersystem crossing followed by ring closure of diradical adduct I is more rapid than intersystem crossing and chlorine migration, in whatever order these steps required for rearrangment occur.

Reaction of Fluorenylidene with Mixtures of Butadiene and the 1,2-Dichloroethylenes. The increase in the stereospecificity of cyclopropanation of *cis*-1,2-dichloroethylene and the decrease in the addition with rearrangement observed with the addition of styrene was more marked with butadiene as a competition reagent. Jones and Rettig had observed a dramatic increase in the stereospecificity of fluorenylidene addition to *cis*-2-butene when butadiene was present.[12]

When butadiene (3.4%) is added to solutions of diazofluorene in *cis*- and *trans*-1,2-dichloroethylene before irradiation, 2-vinylspiro[cyclopropane-1,9′-fluorene] (VIII) is formed as a major product (see Table III) and there is a significant decrease in the ratio of rearrangement product V to dichlorocyclopropanes III and IV. The stereospecificity of cyclopropanation increases dramatically for the *cis*-olefin, reaching 95.2 ± 0.7%.

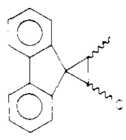
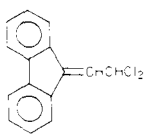
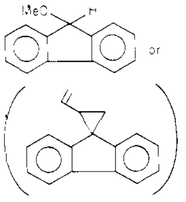


VIII

These experiments clearly indicate that one of the reactive intermediates from irradiation of diazofluorene undergoes stereospecific cis addition to *cis*-1,2-dichloroethylene, while butadiene selectively traps one or more species whose reactions result in the nonstereospecific formation of cyclopropanes III and IV and the rearranged adduct V. These results are similar to those of Jones and Rettig, who worked with butadiene–*cis*-2-butene mixtures,[12] but in the present experiments much smaller concentrations of butadiene are required to increase significantly the stereospecificity of addition to the *cis*-monoolefin.

An interpretation consistent with these facts is that singlet fluorenylidene reacts exclusively by stereospecific cyclopropanation, while triplet fluorenylidene gives a mixture of stereoisomeric cyclopropanes III and IV together with the rearranged adduct V. Earlier results from experiments with diphenylmethylene were subject to the interpretation that a rearranged adduct could be due to reactions of either singlet or triplet carbene, while the cyclopropane formed from addition to *cis*-1,2-dichloroethylene with a high degree of stereoselectivity under all reaction conditions was a product of only the singlet carbene.[7] In the present experiments a decrease in yield of the rearranged adduct V in the presence of butadiene is associated with an increase in the stereospecificity of cyclopropanation. Hence the formation of rearranged adduct is connected with an intermediate undergoing nonstereospecific addition, and therefore likely to be the triplet carbene. Clearly singlet and triplet fluorenylidene are *not* in equilibrium in the presence of even small amounts of butadiene, since the ratios of products to the two carbene spin states vary

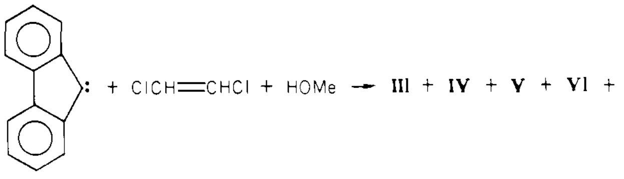
Table III. Irradiation of 9-Diazofluorene (DFL) in Mixtures of 1,2-Dichloroethylene and Methanol or Butadiene

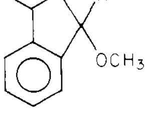
reactants			product yields, % (absolute)				
mol % of $C_2H_2Cl_2$	mol % of additive	initial concn of DFL, mol L^{-1}	 III + IV	 V	 VIII	stereospecificity of cyclopropanation (III)(100)/(III + IV) or [(IV)(100)/(III + IV)]	(V)(100)/(III + VI)
98.7% (cis)	1.25% MeOH	0.069	14.4 ± 0.8	0	30.0 ± 0.8	83.8 ± 0.5	0
99.4% (cis)	0.6% MeOH	0.063	25.5 ± 1.6	0	32.1 ± 1.8	83.6 ± 0.5	0
98.7% (trans)	1.25% MeOH	0.060	16.4 ± 0.8	11 ± 2	27.9 ± 1.6	[93.2 ± 0.1]	67 ± 13
96.6% (cis)	3.4% butadiene	0.048	20.6 ± 0.7	0	(45.1 ± 1.7)	95.7 ± 0.3	0
96.6% (trans)	3.4% butadiene	0.048	16.6 ± 0.7	5 ± 1	(53.8 ± 0.3)	[93.8 ± 1.1]	30 ± 6
48.3% (trans) + 48.3% (cis)	3.4% butadiene	0.070	26.6 ± 1.2	0	(65.4 ± 1.6)	[60.1 ± 0.4]	0

with butadiene concentration. This implies that the rate of reaction of triplet fluorenylidene with butadiene is more rapid than triplet–singlet intersystem crossing.

From the reduction in yields of dichlorocyclopropane products III and IV in the presence of butadiene, it can be estimated that butadiene is ca. 67 times as reactive as *cis*-1,2-dichloroethylene and ca. 86 times as reactive as the trans isomer toward singlet fluorenylidene. From the yield ratio for products VIII vs. V an even higher relative reactivity can be deduced for butadiene toward triplet fluorenylidene. In the presence of only the 1,2-dichloroethylenes, or other substances of much lower reactivity than butadiene, spin-state equilibration may be possible.

Reaction of Fluorenylidene with Mixtures of Methanol and the 1,2-Dichloroethylenes. In contrast with the competition experiments employing butadiene, thought to compete effectively for triplet carbenes, addition of 1.2% methanol, considered to be an efficient trapping agent for singlet carbenes, to solutions of diazofluorene in *cis*- and *trans*-1,2-dichloroethylene before irradiation did not alter the stereospecificity of cyclopropanation (see Table III). That methanol, which is 140 to 200 times as reactive toward fluorenylidene as the 1,2-dichloroethylenes, does *not* affect the ratio of cyclopropanes[27] formed from fluorenylidene and the dichloroethylenes, while the somewhat less reactive butadiene does perturb the ratio, may be due to the selectivity of methanol for the more reactive singlet carbene and butadiene for the less reactive triplet. In the presence of methanol, 9-methoxyfluorene (IX) is a major product.





IX

Since the stereospecificity of cyclopropanation of *cis*-1,2-dichloroethylene by fluorenylidene is unperturbed by the presence of methanol, singlet-to-triplet interconversion of the carbene spin states appears to be more rapid than the reaction of singlet fluorenylidene with methanol. If methanol were equally reactive toward both carbene spin states, the stereospecificity would also be unaffected, but the reactions of triplet carbenes with methanol should lead to formal C-H insertion via an abstraction–recombination mechanism.[28]

Reaction of Fluorenylidene with Mixtures of *cis*-Dichloroethylene, Hexafluorobenzene, and Butadiene. Our final series of experiments employed various diluents to determine whether they would influence the ratios of products formed from irradiation of diazofluorene in the presence of *cis*-1,2-dichloroethylene.

Jones and Rettig had found that dilution of diazofluorene–*cis*-2-butene mixtures with hexafluorobenzene led to a decrease in the ratio of *cis*- to *trans*-2,3-dimethylspiro[cyclopropane-1,9′-fluorene] formed.[12] This was attributed to a decrease, due to dilution, of the rate of singlet fluorenylidene addition to the olefin relative to the rate of singlet-to-triplet relaxation by the carbene. The alteration of stereospecificity implied that the rate of reaction with olefin was more rapid than spin-state interconversion even when the concentration of olefin was only ca. 1 M.

When diazofluorene is irradiated in mixtures of hexafluorobenzene and *cis*-1,2-dichloroethylene the stereospecificity of cyclopropanation decreases with increasing concentrations of hexafluorobenzene, from 86% with no hexafluorobenzene to 41% at 0.8 mol fraction of diluent, and the relative yield of rearrangement product V increases (see Table IV). Since the absolute yield of *trans*-cyclopropane IV actually increases with added hexafluorobenzene, the change in the stereospecificity of cyclopropanation is likely to be due to an effect other than selective scavenging of a reactive intermediate. Reaction of fluorenylidene with hexafluorobenzene does, however, certainly occur and is discussed further below. Griller et al. reported the formation of a 1:1 adduct in 20% yield, but also found that the lifetime of the 470-nm transient observed in laser flash experiments and believed due to triplet fluorenylidene has a longer lifetime in hexafluorobenzene than in other fluid media, acetonitrile, and cyclohexane.[21] We have found a mixture of more than two fluorenylidene–hexafluorobenzene adducts, and their structures are being elucidated.[29] In the present experiments the yield of bifluorenylidene (VI) also increases with increasing concentration of hexafluorobenzene.

The addition of butadiene to solutions of diazofluorene in 4:6 mixtures of hexafluorobenzene and *cis*-1,2-dichloroethylene prior to irradiation has a marked effect (see Table V). At a butadiene:*cis*-1,2-dichloroethylene mol ratio of only 0.003 the yield of butadiene adduct VIII is nearly equal to the sum of the yields of the dichloroethylene adducts III–V. Even at this low concentration of butadiene an increase in stereospecificity can be discerned, the fraction of *cis*-dichlorocyclopropane III/(III + IV) having increased to 74% from 62 to 69% in the absence of butadiene. The stereospecificity increases to 88% at a butadiene:dichloroethylene mol ratio of 0.025. The yield of rearranged dichloroethylene adduct V is reduced about twice as efficiently

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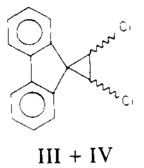
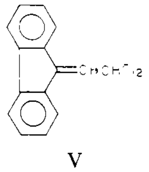
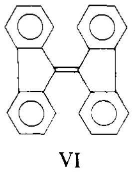
(27) Rearranged adduct V undergoes reaction with methanol, presumably by nucleophilic displacement.

(28) H. Tomioka and Y. Izawa, *J. Am. Chem. Soc.*, **99**, 6128 (1977).

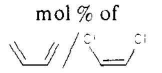
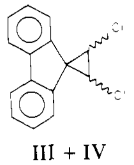
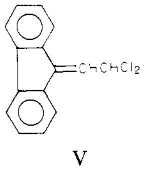
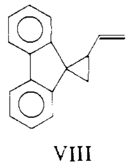
(29) Characterization of the stable products from reactions of fluorenylidene with hexafluorobenzene is being carried out in collaboration with Professor Maitland Jones, Jr., Princeton University.

Table IV. Irradiation of 9-Diazofluorene (DFL) in Mixtures of *cis*-1,2-Dichloroethylene and Hexafluorobenzene (HFB)

reactants		product yields, % (absolute)				
mol % of HFB	initial concn of DFL, mol L^{-1}	 III + IV	 V	 VI	stereospecificity of cyclopropanation (III)(100)/(III + IV)	(V)(100)/ (III + IV)
0	0.051	41.4 ± 1.1	10 ± 2	8.7 ± 0.9	86.4 ± 0.5	24 ± 5
20	0.067	19.6 ± 0.9	10 ± 2	5.5 ± 0.6	78.7 ± 1.4	51 ± 10
30	0.066	20.0 ± 0.4	8 ± 2	8.9 ± 0.9	74.4 ± 0.9	40 ± 10
40	0 064	39.0 ± 1.4	23 ± 5	13.2 ± 1.3	69.1 ± 0.8	59 ± 13
40	0.050	40.0 ± 2.0	31 ± 6	*a*	62.0 ± 0.5	78 ± 15
60	0.067	17.4 ± 1.6	8 ± 2	17.7 ± 1.8	60.0 ± 0.6	46 ± 12
80	0.050	23.9 ± 0.5	15 ± 3	20.8 ± 2.1	41.2 ± 0.6	63 ± 13

[a] Not determined.

Table V. Irradiation of 9-Diazofluorene (DFL) in a 4:6 Mixture of Hexafluorobenzene and *cis*-1,2-Dichloroethylene and Butadiene

reactants		product yields, % (absolute)				
mol % of 	initial concn of DFL, mol L^{-1}	 III + IV	 V	 VIII	stereospecificity of cyclopropanation (III)(100)/(III + IV)	(V)(100)/ (III + IV)
0[a]	0.064	39.0 ± 1.4	23 ± 5	0	69.1 ± 0.8	59 ± 13
0	0.050	40.0 ± 2.0	31 ± 6	0	62.0 ± 0.5	78 ± 15
0.30	0.059	27.8 ± 0.7	13 ± 3	26.9 ± 0.8	74.0 ± 1.0	47 ± 11
0.50	0.065	21.4 ± 1.1	7 ± 2	41.2 ± 1.8	76.1 ± 1.1	33 ± 9
0.75	0.060	19.4 ± 0.9	5 ± 1	54.7 ± 2.9	78.1 ± 0.4	26 ± 5
1.5	0.060	8.7 ± 0.3	trace	52.5 ± 2.5	84.2 ± 0.6	
2.5	0.076	8.7 ± 0.6	trace	75.0 ± 3.2	88.1 ± 1.0	

[a] 13.2% absolute yield of bifluorenylidene (VI) also detected.

as that of cyclopropane products III + IV by the presence of butadiene.

On the basis of these yields reductions, butadiene is ca. 200 times as reactive as *cis*-1,2-dichloroethylene toward the species giving rise to dichlorocyclopropanes III and IV and ca. 400 times as reactive toward the intermediate that forms rearranged adduct V. Judged from the ratio of product yields (as opposed to individual yield reductions) butadiene is ca. 300 times as reactive as *cis*-1,2-dichloroethylene toward the mixture of reactive intermediates formed from diazofluorene. This is a considerable increase over the reactivity ratio of ca. 100 observed in butadiene–dichloroethylene mixtures in the absence of hexafluorobenzene.

It is clear that there is more than one product-forming intermediate that arises from irradiation of diazofluorene in mixtures of hexafluorobenzene and *cis*-1,2-dichloroethylene. The species that yields *cis*-dichlorocyclopropane III decreases in importance with increasing hexafluorobenzene concentration; indeed Figure 1 indicates that the decrease in stereoselectivity is a nearly linear function of the hexafluorobenzene concentration.

The species undergoing cis addition can reasonably be identified as singlet fluorenylidene. If the role of hexafluorobenzene were solely as an inert diluent and moderator, the species that undergoes nonstereospecific cyclopropanation and also yields rearrangement product V[30] could be confidently identified as triplet fluorenylidene.

Hexafluorobenzene is, however, certainly *not* inert toward fluorenylidene. Since stable products have been isolated, if not identified,[21,29] one may ask whether fluorenylidene could react *reversibly* with hexafluorobenzene to form a complex or adduct whose dissociation could be a new path for singlet–triplet relaxation.[31,32] A short-lived fluorenylidene–hexafluorobenzene complex might alternatively act as a *carbenoid*, undergoing reaction with olefins.

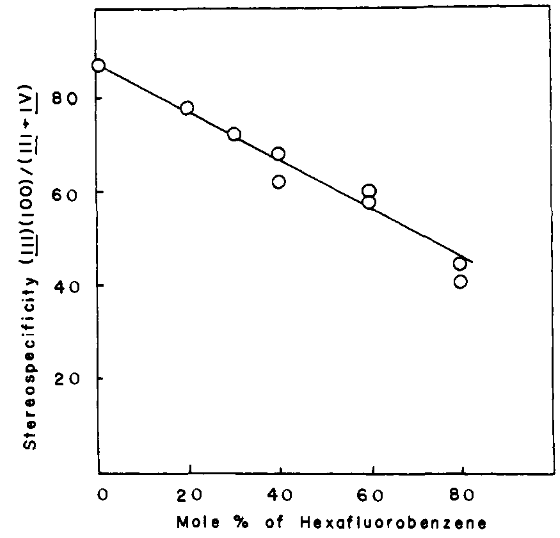


Figure 1. Stereospecificity of addition of fluorenylidene to *cis*-1,2-dichloroethylene in mixtures with hexafluorobenzene.

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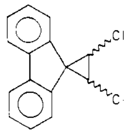
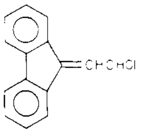
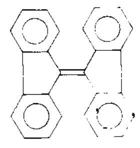
[30] Since the ratio of *trans*-2,3-dichlorospiro[cyclopropane-1,9′-fluorene] (IV) to rearranged adduct V formed from *cis*-1,2-dichloroethylene is a nearly constant 2:3, both these products may be presumed to arise from the same intermediate.

[31] Such a process would be reminiscent of the Schenk mechanism for photochemical energy transfer: G. O. Schenk and R. Steinmetz, *Tetrahedron Lett.*, *21*, 1 (1960).

[32] Any substrate possessing a π bond or a lone pair of electrons could in principle react with a carbene to form a carbenoid. The case for hexafluorobenzene is particularly strong since in its presence (but not that of other fluorocarbons nor of benzene) the yield of *trans*-cyclopropane IV from *cis*-1,2-dichloroethylene increases. This is evidence for the formation of a carbenoid not yet found for other unsaturated substrates.

Table VI. Irradiation of 9-Diazofluorene (DFL) in Mixtures of *cis*-1,2-Dichloroethylene and Various Diluents

reactants			products yields, % (absolute)				
							
mol % of *cis*-$C_2H_2Cl_2$	mol % of diluents	initial concn of DFL, mol L^{-1}	III + IV	V	VI	stereospecificity of cyclopropanation (III)(100)/(III + IV)	(V)(100)/(III + IV)
60	Freon-113, 40	0.063	20.9 ± 0.3	7 ± 2	24.4 ± 2.5	83.6 ± 0.8	33 ± 10
40	Freon-113, 60	0.062	17.8 ± 0.7	8 ± 2	28.2 ± 2.8	79.4 ± 1.0	45 ± 11
40	C_7H_{14}, 33 Freon-113, 27	0.062	11.2 ± 0.4	*a*	25.2 ± 2.5	77.3 ± 1.0	*a*
38	C_7F_{14}, 24 Freon-113, 38	0.061	7.9 ± 0.3	*a*	18.7 ± 1.9	77.2 ± 0.4	*a*
60	Me_4Si, 40	0.061	30.5 ± 0.8	5 ± 1	12 ± 1.2	82.6 ± 0.5	16 ± 3
40	Me_4Si, 40	0.064	16.6 ± 0.6	*a*	12 ± 1.2	79.4 ± 1.4	*a*
40	Me_4Si, 60	0.064	15.0 ± 0.6	*a*	12 ± 1.2	77.1 ± 0.6	*a*
60	C_6H_6, 40	0.065	29.6 ± 0.7	10 ± 2	*a*	84.2 ± 0.3	34 ± 7
40	C_6H_6, 60	0.064	17.8 ± 0.5	9 ± 2	*a*	82.7 0.7	51 ± 11

[a] Not determined

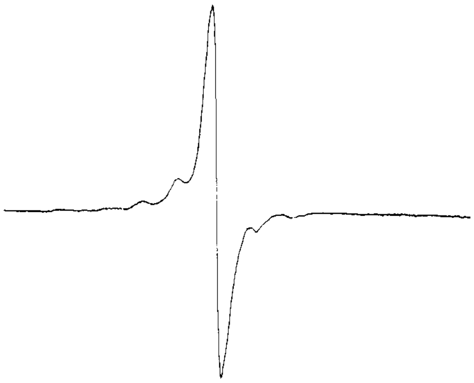
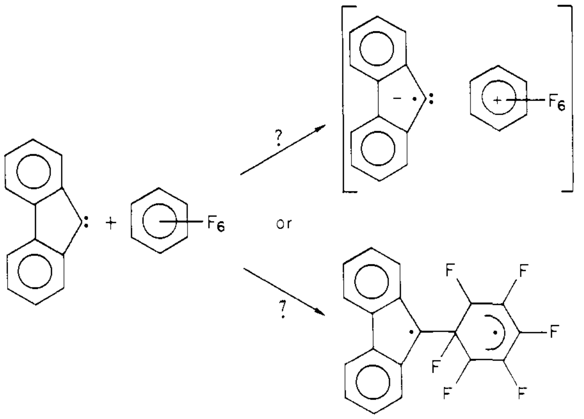


Figure 2. Electron spin resonance spectrum following irradiation of a 3.5 wt % mixture of diazofluorene in hexafluorobenzene at −127 ± 1 °C. The signal is centered at 3250 G, and a total width of 500 G is displayed.

An Electron-Spin Resonance Experiment. Evidence for radical intermediates formed from fluorenylidene and hexafluorobenzene has been found in an ESR experiment. Irradiation of a 3.5% solution of diazofluorene in hexafluorobenzene frozen and cooled to −127 ± 1 °C in the microwave cavity of an EPR spectrometer gave rise not to the well-known ESR spectrum of triplet fluorenylidene formed in other matrices but to the spectrum shown in Figure 2. Warming of the matrix successively to −60, −55, and −40 °C led to a decrease in signal intensity without change in line shape. Further warming led to the disappearance of the signal, which is thus due either to a mixture of monoradicals that are lost at the same rate or to a single diradical (with a rather weak dipolar interaction of the unpaired electrons). Repetition of the experiment at −196 °C yields ESR signals only after prolonged irradiation, after which a weak spectrum of triplet fluorenylidene[33] is visible together with a single narrow doublet-radical signal. While irradiation of pure frozen hexafluorobenzene produces no detectable ESR signal, the hexafluorobenzene is involved in the process leading to the signal observed from diazofluorene–hexafluorobenzene mixtures. This is apparent since irradiation of a frozen diazofluorene–perfluorotoluene mixture produces quite a different ESR spectrum.

The ESR spectrum of Figure 2 does not lend itself to ready interpretation; neither a radical anion–radical cation complex formed by electron transfer nor a covalently bonded diradical adduct seems entirely compatible with it. The spacing between the outer peaks in the spectrum of Figure 2, ca. 37 G, is larger than the 15.9-G spacing between the seven lines of the hexafluorobenzene radical cation,[34] whose fluorine hyperfine coupling constant is that expected for a π-radical cation.[35] The hexafluorobenzene radical anion, however, gives an ESR spectrum that is ca. 800 G wide in methyltetrahydrofuran glass at 77 K[36] due to an extraordinarily large coupling constant a_F = 137 G, which is an order of magnitude larger than that expected for a π-radical anion.[35] Both a planar σ* radical[35,37] and a nonplanar structure with both σ and "pseudo π" delocalization[36] have been suggested to explain the large fluorine hyperfine coupling in $C_6F_6^{-}\cdot$.



Examination of the effects of other relatively inert molecules on the product distribution from diazofluorene and *cis*-1,2-dichloroethylene also suggested that the role of hexafluorobenzene is *not* simply as a diluent. See Table VI.

Reactions of Fluorenylidene in Mixtures of *cis*-1,2-Dichloroethylene and 1,1,2-Trichlorotrifluoroethane, Perfluoromethylcyclohexane, Tetramethylsilane, or Benzene. When mixtures of diazofluorene and *cis*-1,2-dichloroethylene are diluted with 1,1,2-trichlorotrifluoroethane (Freon 113), there is very little effect on the stereospecificity of cyclopropanation at the mole fraction of diluent (0.4 and 0.6) at which there was a significant decrease in stereospecificity in the presence of hexafluorobenzene. In the Freon experiments the yields of olefin adducts III–V decrease and the yield of bifluorenylidene (VI) increases, presumably because the diazofluorene competes more effectively for fluorenylidene

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as the ratio of diazofluorene to *cis*-1,2-dichloroethylene increases. Benzene had a similar and even smaller effect on the stereospecificity of cyclopropanation as the Freon, and in the presence of mixtures of Freon and perfluoromethylcyclohexane there is only a small change in stereospecificity, but a greater reduction in cyclopropane yields.

Even tetramethylsilane can be used as a reasonably inert diluent; again the stereospecificity of cyclopropanation is essentially the same as in undiluted *cis*-1,2-dichloroethylene.

It is thus clear that neither simple dilution nor merely the presence of fluorine atoms alters the stereospecificity of reaction of diazofluorene and *cis*-1,2-dichloroethylene. The observed lack of effect on the stereospecificity of cyclopropanation of the saturated fluorocarbons, benzene, and tetramethylsilane can be explained by a constant ratio of singlet and triplet carbene concentrations in the presence of these molecules. This constancy could be due either to a rate of intersystem crossing slow compared to the rate of reaction with dichloroethylene or to a spin-state interconversion rapid relative to reaction rates.

Hexafluorobenzene does alter the product ratios, and has an effect quite different from that of the highly reactive substrate butadiene, in whose presence the cyclopropanation of *cis*-1,2-dichloroethylene becomes more stereospecific and the relative yields of rearranged adduct V drop. While hexafluorobenzene may be exerting a solvent effect, changing the ratio of rapidly interconverting singlet and triplet fluorenylidenes by altering the free-energy difference by differential solvation, reversible complexation or chemical combination seems more likely. The detection of radical intermediates and stable products from diazofluorene and hexafluorobenzene also supports this interpretation.

Conclusions

The photolysis of diazofluorene in *cis*-1,2-dichloroethylene produces two different reactive intermediates, one of which undergoes stereospecific cyclopropanation, while the other gives a mixture of *cis*- and *trans*-cyclopropanes III + IV and an adduct V whose formation is most easily explained if it arises by rearrangement of a diradical intermediate I. These two reactive intermediates are believed to be singlet and triplet fluorenylidene, respectively, and their interconversion appears to be slow relative to the rate of reaction of at least one of them with butadiene, which is ca. 10^2 more reactive toward fluorenylidene than the dichloroethylenes.

While methanol is also more reactive toward fluorenylidene than are the dichloroethylenes, the stereospecificity of cyclopropanation of *cis*-1,2-dichloroethylene is not altered by its presence. This may be due to selective scavenging of singlet fluorenylidene by methanol, while butadiene is more efficient in trapping the triplet carbene. The singlet-to-triplet intersystem crossing of fluorenylidene appears to be more rapid than the reactions of the singlet with methanol and hence its reactions with *cis*-1,2-dichloroethylene.

The ability of hexafluorobenzene to reduce the stereospecificity of cyclopropanation may be due to the formation of a diradical adduct that can act as a carbenoid.

It is now clear that *cis*-dichloroethylene does not react with every triplet carbene to give exclusively rearranged adducts. In the case of fluorenylidene, the initial adduct of the triplet carbene and the dichloroethylene seems to be a diradical that undergoes partitioning between rearrangement and cyclization, the former process predominating for the *cis*-olefin. The present studies indicate that singlet fluorenylidene does not react with the 1,2-dichloroethylenes by a stepwise addition.

Experimental Section

General. Routine nuclear magnetic resonance (NMR) spectra were recorded on a Hitachi Perkin-Elmer R-24B instrument, while a JEOL JNM-FX100 Multinuclear 100 MHz FT spectrometer was employed for ^{13}C spectra. Electron spin resonance (ESR) spectra were recorded with a Varian E-3 instrument. Reaction mixtures were irradiated in situ in the microwave cavity of the ESR spectrometer with an Eimac 150-W xenon lamp filtered with Pyrex glass and water. The samples were maintained at 77 K in a transparent quartz Dewar with liquid nitrogen and at higher temperatures in a double-walled evacuated cylindrical quartz insert with a flowing cold nitrogen gas stream. Temperature measurements in the ESR cavity were made with a thermocouple.

Yields. In most cases reported yields were determined by ^{1}H NMR integration relative to toluene or benzaldehyde which was added as an internal standard just prior to analysis.

Preparation of 9-Diazofluorene. The procedure of Moss and Joyce was followed.[13]

***cis*-1,2-Dichloroethylene.** The bromine-catalyzed photoisomerization of *trans*-1,2-dichloroethylene yielded, upon fractional distillation, the cis isomer containing 0.5% trans isomer and <0.5% chloroform.[6,38]

Preparation of 9-(2,2-Dichloroethylidene)fluorene (V). 2-((9-Hydroxyfluorenyl)methyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine. In a three-necked flask equipped with a magnetic stirrer, addition funnel, and N_2 gas inlet, a solution of 17.1 g (50 mmol) of 2,4,4,6-tetramethyl-5,6-dihydro-1,3-oxazine[39] in 50 mL of dry tetrahydrofuran (THF) was cooled to −78 °C. To the stirred solution was added dropwise 35 mL of 1.6 M (55 mmol) *n*-butyllithium in hexane over a period of 1 h. To the yellow reaction mixture was added slowly a solution of 10.3 g (57 mmol) of fluorenone in 12 mL of THF. The mixture was then allowed to warm to room temperature, poured into excess ice and water, acidified with 9 N HCl, extracted three times with pentane, made basic with 40% aqueous KOH, and finally extracted with ether. After being dried over K_2CO_3, evaporation of the ether left the oxazine in a crude yield of 61%. Recrystallization from *n*-hexane yielded a pure product: mp 114 °C; ^{1}H NMR ($CDCl_3$) δ 1.02–1.90 (m, 12 H, oxazine hydrogens), 2.5 (s, 2 H, CH_2), 4.05 (br, 1 H, OH) 7.1–7.75 (m, 8 H, aromatic); IR (KBr) 3220 (m), 2980 (s), 2938 (m), 1652 (s, d), 1608 (w), 1450 (s), 1380 (m), 1360 (s), 1322 (s), 1240 (s), 1208 (s), 1197 (s), 1148 (s), 1050 (s), 770 (s), 745 cm^{-1} (s); MS (70 eV) *m/e* 321 (P, 2.7) 181 (82.5), 180 (99.3), 153 (41.6), 152 (99.8), 150 (83.6), 141 (base, 100), 126 (92.0) 99 (99.8).

2-((9-Hydroxyfluorenyl)methyl)-4,4,6-trimethyl-2,3,5,6-tetrahydro-1,3-oxazine. To a magnetically stirred mixture of 10.5 g (32.7 mmol) of crude dihydrooxazine, 50 mL of THF, and 50 mL of 95% ethanol in a conical flask, cooled to −30 °C in a dichloroethane–dry ice slush bath, 9 N HCl was added dropwise until the pH was 7. Solutions of sodium borohydride (1.89 g in 2 mL of H_2O) and 40% aqueous KOH were added alternately to maintain a pH 6 to 8. The reaction mixture was then poured into 50 mL of H_2O and made basic by addition of further 40% aqueous KOH. After separation of the organic layer, the aqueous phase was extracted several times with ether, whose evaporation gave 10.2 g (97%) of crude product. Two recrystallizations from *n*-hexane gave colorless crystals: mp 103 °C; ^{1}H NMR ($CDCl_3$) δ 1.05–1.65 (m, 12 H, oxazine CH_3, CH_2, 6-CH), 2.04 (d, 2 H, $J = 5.0$ Hz, 1′-CH_2), 3.80 (m, >1 H, OH and possibly NH), 4.80 (t, 1 H, $J = 5.0$ Hz, 2-OCHN), 7.15–7.70 (m, 8 H, aromatic); IR (KBr) 3250 (br, s), 2972 (s), 2960 (m), 2920 (m) 2900 (m), 1608 (m), 1450 (s), 1205 (s), 1020 (s), 830 (m), 775 (s), 738 cm^{-1} (s); MS (70 eV) *m/e* 323 (P, 4.5), 181 (39.9), 180 (base, 100), 253 (23.6), 152 (98.8), 151 (65.6), 150 (46.1), 128 (95.7).

Fluoreneylideneacetaldehyde. A mixture of 9.5 g (29.4 mmol) of crude tetrahydrooxazine, 27 g (0.3 mol) of oxalic acid, and 75 mL of water was refluxed for 40 min, cooled, and extracted with three 10-mL portions of ether. Evaporation of the ether from the combined extracts dried over K_2CO_3 gave 5.4 g (89%) of crude fluorenylidenacetaldehyde. Recrystallization from petroleum ether gave yellow needles: mp 116 °C (lit.[40] mp 116–117 °C); ^{1}H NMR ($CDCl_3$) δ 6.78 (d, 1 H, $J = 8.0$ Hz, C=CH), 7.1–8.1 (m, 8 H, aromatic), 10.8 (d, 1 H, $J = 8.0$ Hz, CH=O).

9-(2,2-Dichloroethylidene)fluorene (V). To a solution of 3 g (14.5 mmol) of fluorenylideneacetaldehyde in 15 mL of CCl_4 cooled to −10 °C in an ice–salt bath, 3.4 g (16.4 mmol) of PCl_5 was added in portions over a 25-min period. After warming slowly to room temperature the mixture was poured on crushed ice and quickly extracted with three 5-mL portions of CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and the solvent removed in vacuo leaving 3.5 g of a brown oil (crude yield 92%) that was recrystallized from methylene chloride–pentane at −34 °C to give a brown solid: mp 35–37 °C; ^{1}H NMR ($CDCl_3$) δ 6.71 (d, 1 H, $J = 12$ Hz), 7.08–7.73 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 66.9 ($CHCl_2$), 119.7, 120.2, 120.9, 124.8, 125.7, 126.6, 127.4, 129.4, 129.6, 134.7, 136.5, 137.6, 139.8, 141.7; MS (70 eV) m/e 264 (1.2), 263 (2.1), 262 (3.0), 261 (2.1), 260 (6.7), 227 (13), 225 (40), 206 (97.1), 205 (85.8), 191 (32), 189 (40), 165 (100), 152 (39.2), 151 (36.8).

Partial hydrolysis of 9-(2,2-dichloroethylidene)fluorene (V) to Fluorenylideneacetaldehyde. Spectral interferences discouraged the use of ^{1}H NMR spectroscopy for determining the yield of product V from addition of fluorenylidene to the 1,2-dichloroethylenes. Therefore hydrolysis of

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V to fluorenylideneacetaldehyde was undertaken, since no other peaks appeared near the aldehydic proton. Product mixtures from 250 mg (1.30 mmol) of diazofluorene were dissolved, after ^{1}H NMR assay of the cyclopropane, and bifluorenylidene products III, IV, and VI, in 1 mL of dimethyl sulfoxide (Me_2SO) and $^1/_4$ mL of H_2O added. This mixture was stirred in the dark for 15 h. After addition of 5 mL of CH_2Cl_2 the mixture was extracted with 10 mL of water, which removed the Me_2SO. After removal of the CH_2Cl_2 in vacuo, the residue was dissolved in $CDCl_3$ and again subjected to ^{1}H NMR spectroscopy. Control experiments indicated that 33% of V was consistently converted to aldehyde and 67% was recovered. The cyclopropane products III and IV were recovered unchanged. Therefore the yields of fluorenylideneacetaldehyde obtained upon partial hydrolysis were multiplied by three to obtain the yields of V. The validity of this chemical derivatization method for the analysis of V was checked by comparison with direct ^{13}C NMR analysis of V. The agreement was ±20%, and this is used to estimate the probable error of the hydrolysis method. At higher temperatures, and with catalysis by added acid or base, higher conversions of V to aldehyde can be obtained, but only at the expense of partial destruction of the cyclopropane products III and IV, which would provide an additional source of aldehyde and would in the end render the analysis of V unreliable.

Irradiation of Diazofluorene in *trans*- or *cis*-1,2-Dichloroethylene. A solution of 1 g (5.2 mmol) of diazofluorene and 150 mL of *trans*-1,2-dichloroethylene was placed in a Pyrex outer jacket surrounding a quartz immersion well. After being purged with a dry nitrogen gas stream for 2 h, the solution was irradiated for 24 h with a Hanovia 450-W medium-pressure mercury lamp placed within the water-cooled immersion well and shielded by a cylindrical uranium glass filter to remove all wavelengths below 330 nm. After removal of dichloroethylene and other volatiles by evaporation in vacuo, the reaction mixture was subjected to chromatography on a 1 × 6 in. column of silica gel 60, 230–400 mesh (Taylor Chemical Co.), with *n*-hexane as eluent. *trans*-2,3-Dichlorospiro[cyclopropane-1,9′-fluorene] (IV) was isolated as the major product from the first fraction (TLC, R_f value 0.44) formed in 31 to 44% yield, mp 112 °C. A pure sample was obtained by recrystallization from 10% chloroform in hexane: ^{1}H NMR ($CDCl_3$) δ 4.17 (s, 2 H, CHCl), 7.2–7.8 (m, 8 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 41.6, 47.4, 120.0, 123.0, 126.9, 128.0, 140.6, 141.4; IR (KBr) 3040 (w), 1480 (m), 1450 (s), 1442 (s), 1350 (m), 1243 (s), 843 (s), 830 (s), 742 (vs), 640 cm^{-1} (s); MS (70 eV) *m/e* 264 (1.5), 262 (4.6), 260 (8.6), 227 (26.5), 225 (77.7), 190 (34.5), 189 (100), 188 (16.8), 187 (20.7). Anal. Calcd for $C_{15}H_{10}Cl_2$: C, 68.99; H, 3.86; Cl, 27.15. Found: C, 69.07; H, 3.95; Cl, 27.36. Bifluorenylidene (VI) was obtained as the second fraction eluted (TLC Rf value 0.40) in 6 to 9% yield as red needles, mp 188–189 °C (lit.[41] mp 187–189). The third fraction (TLC R_f value 0.37) yielded 4 to 7% of *cis*-2,3-dichlorospiro[cyclopropane-1,9′-fluorene] (III), mp 148–149 °C, identical in its properties with the major product obtained in 30 to 35% yield from the reaction of diazofluorene with *cis*-1,2-dichloroethylene: ^{1}H NMR ($CDCl_3$) δ 4.09 (s, 2 H, CHCl), 6.8–7.8 (m, 8 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 38.2, 43.8, 118.5, 120.1, 126.4, 126.9, 127.3, 127.4, 131.6, 138.0; IR (KBr) 3022 (w), 1480 (m), 1443 (s), 1331 (m), 1260 (s), 882 (s), 752 (s), 738 (s), 672 cm^{-1} (m); MS (70 eV) *m/e* 264 (1.7), 262 (3.4), 260 (4.8), 227 (24.1), 225 (84.4), 190 (34), 189 (100), 188 (18.0). Anal. Calcd for $C_{15}H_{10}Cl_2$: C, 68.99; H, 3.86; Cl, 27.15. Found: C, 68.88; H, 4.11; Cl, 27.24.

The stereospecificity of cyclopropanation was determined in small-scale reactions. Solutions of 250 mg (1.30 mmol) of diazofluorene in 20 mL of 1,2-dichloroethylene were placed in 18 × 280-mm pyrex tubes with necks constricted for sealing after 3 freeze–pump–thaw cycles on a vacuum line. The sealed tubes were mounted next to the immersion well and irradiated as described above. Product mixtures were isolated by removal of dichloroethylene under vacuum and dissolved in $CDCl_3$ for ^{1}H NMR analysis, with 5.0 μL of toluene added as an internal standard. Yields of products III, IV, and VI were determined from integration of peaks at δ 4.09 (CHCl for III), 4.17 (CHCl for IV), and 8.15–8.45 (2 H's of VI), respectively. The yield of V was obtained by integration of its aldehyde proton at δ 10.8 after partial hydroglysis, as described above.

Irradiation of Diazofluorene in Styrene. A solution of 200 mg (1.0 mmol) of diazofluorene in 20 mL of styrene was irradiated in a degassed sealed Pyrex ampule as described above. After removal of excess styrene in vacuo, yellow crystals were observed, but thin-layer chromatography indicated the presence of a small amount of a second component in addition to the major product, 2-phenylspiro[cyclopropane-1,9′-fluorene] (VII), isolated by elution with 20% benzene in hexane from a silica gel column in 92% yield (246 mg): mp 127 °C (lit.[42] mp 130–131); ^{1}H NMR ($CDCl_3$) δ 2.10 (d, 2 H, J = 9 Hz, CH_2), 3.28 (t, 1 H, J = 9 Hz, CHPh), 6.1–7.9 (m, 13 H, aromatic).

Irradiation of Diazolfluorene in Mixtures of Styrene and 1,2-Dichloroethylenes. In a series of experiments 100 to 142 mg (0.51 to 0.74 mmol) of diazofluorene was dissolved in 10 mL of *trans*- or *cis*-1,2-dichloroethylene and amounts of styrene varying from 37.5 to 750 μL (0.25 to 5.0 mol %) were added and the reaction tubes degassed, sealed, and irradiated as described above. The aldehyde proton peak of benzaldehyde at δ 10.0 was the internal standard against which product yields were determined. The results are given in Tables I and II.

Irradiation of Diazofluorene in Mixtures of Methanol or Butadiene with 1,2-Dichloroethylenes. In experiments with added methanol ca. 1.1 mmol (216 mg) of diazofluorene, 16 mL of dichloroethylene, and 25 or 50 μL (0.62 or 1.23 mol %) of methanol were employed. In addition to the cyclopropanation products III and IV, 9-methoxyfluorene (IX) was observed by ^{1}H NMR spectroscopy and characterized by its absorptions at ($CDCl_3$) δ 3.05 (s, OCH_3), 5.52 (s, CHOMe), and 7.0–7.8 (m, aromatic); these values agree with reported values.[43] Yields were determined by integration relative to a toluene internal standard.

In experiments with butadiene, gaseous butadiene was condensed in a calibrated tube on the vacuum line and evaporated and recondensed on top of a frozen, degassed solution of diazofluorene in 1,2-dichloroethylene. After sealing and thawing the tubes were shaken to mix the contents. In addition to the products from diazofluorene and dichloroethylene, 2-vinylspiro[cyclopropane-1,9′-fluorene] (VIII) was identified as a major product by its ^{1}H NMR spectrum: ($CDCl_3$) δ 2.0 (m, cyclopropyl), 2.60 (q, ABX, J_{AX} = 9 Hz, J_{BX} = 7 Hz, allylic cyclopropyl), 5.15, 5.22, 5.90 (m, vinyl); this agreed with the literature.[44] Yields were obtained by integration relative to a benzaldehyde internal standard. Results are given in Table III.

Irradiation of Diazofluorene in Mixtures of *cis*-1,2-Dichloroethylene and Hexafluorobenzene. In one series of experiments the mole fraction of hexafluorobenzene was varied, keeping the concentration of diazofluorene nearly constant (0.050–0.067 M). In another series a constant ratio of hexafluorobenzene to dichloroethylene (4:6) was employed, together with 0.050–0.076 M *cis*-1,2-dichloroethylenes, but wiih varying amounts of butadiene (0.30 to 2.5 mol %) added as described above. Results are given in Tables IV and V.

Irradiation of Diazofluorene in Mixtures of *cis*-1,2-Dichloroethylene and Various Diluents. 1,1,2-Trichlorotrifluoroethane (Freon-113), perfluorocyclohexane, tetramethylsilane, and benzene were employed as diluents for solutions of diazofluorene in *cis*-1,2-dichloroethylene. All these diluents were added as liquids to the reaction mixtures that were then processed as previously described. Results are given in Table IV.

Control Experiments. It was demonstrated that no reactions occurring in the absence of light contribute to formation of the observed products. ^{1}H NMR analysis of unirradiated reaction mixtures indicated that no decomposition of diazofluorene had taken place. Gas-chromatographic analyses demonstrated that no cis–trans isomerization of the 1,2-dichloroethylenes took place on the time scale of the photolysis experiments. The stability of products III, IV, and V under photolysis conditions was demonstrated in experiments in which pure samples of each were irradiated in 1,2-dichloroethylene solutions. The stability of the cyclopropane products III and IV under the conditions used to hydrolyze V to fluorenylideneacetaldehyde was also carefully checked.

ESR Experiments. Irradiation of a frozen solution containing 3.5 wt % diazofluorene in hexafluorobenzene at −127 °C for 1 min in situ in the microwave cavity of the ESR spectrometer led to the spectrum centered at 3250 G shown in Figure 2. On warming the irradiated sample from −127 to −60 °C, then to −55 °C, and finally to −40 °C, the signal decayed without changing line shape. Irradiation at −196 °C for 10 min gives only a featureless free-radical signal, but after 25 min of irradiation, a weak triplet fluorenylidene signal was observed at 4400 and 5500 G.[33] Irradiation of a similar frozen solution of diazofluorene in perfluorotoluene at −196 °C for 40 s produced a triplet fluorenylidene signal and a free-radical signal near 3250 G which appears to be a distorted 1:4:6:4:1 quintet.

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Registry No. Diazofluorene, 832-80-4; fluorenylidene, 2762-16-5; *trans*-1,2-dichloroethylene, 156-60-5; *cis*-1,2-dichloroethylene, 156-59-2; 9-(2,2-dichloroethylene)fluorene, 87319-65-1; styrene, 100-42-5; 1,3-butadiene, 106-99-0; hexafluorobenzene, 392-56-3; 1,1,2-trichlorotrifluoroethane, 76-13-1; perfluoromethylcyclohexane, 355-02-2; tetramethylsilane, 75-76-3; benzene, 71-43-2; methanol, 67-56-1; 2,4,4,6-tetramethyl-5,6-dihydro-1,3-oxazine, 26939-18-4; fluorenone, 486-25-9; 2-((9-hydroxyfluorenyl)methyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine, 88687-13-2; 2-((9-hydroxyfluorenyl)methyl)-4,4,6-trimethyl-2,3,5,6-tetrahydro-1,3-oxazine, 88687-14-3; fluorenylidenacetaldehyde, 4425-71-2; *trans*-2,3-dichlorospiro[cyclopropane-1,9′-fluorene], 87319-64-0; *cis*-2,3-dichlorspiro[cyclopropane-1,9′-fluorene], 87319-63-9; 2-phenylspiro[cyclopropane-1,9′-fluorene], 10423-18-4; 2-vinylspiro[cyclopropane-1,9′-fluorene], 57393-06-3.

Thermal and Photochemical Deazetations of Fluorine-Substituted 4-Methylenepyrazolines. The Kinetic Behavior of Trimethylenemethanes

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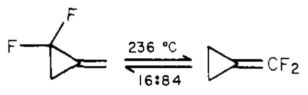
Abstract: 4-(Difluoromethylene)-1-pyrazoline and 4-(fluoromethylene)-1-pyrazoline were observed to undergo thermal and photochemical deazetation in the gas phase as well as in solution to form mixtures of methylenecyclopropanes. The gas-phase and solution-phase, thermal, and photochemical results are contrasted, and the observed kinetically controlled product ratios are compared with the very different equilibrium values. As a result, mechanisms involving trimethylenemethane diradicals are proposed for both processes. The photochemical reactions seem to be dominated by "hot" reactions of vibrationally excited TMM's, while the thermal reactions show interesting selectivity in their cyclization processes.

A recent study of the thermal equilibration of difluoromethylenecyclopropanes **1** and **2** demonstrated a moderate thermodynamic preference of vinylic, substitution over cyclopropyl substitution for geminal fluorine substituents.[1] In short, a substantial geminal destabilization of the fluorine substituents on **1**, coupled with a slight inherent preference of allylic over vinylic geminal fluorine substitution, leads to the observed excess of **2** at equilibrium.[2–5]



1 2

$$\Delta H^\circ = -1.9 \text{ kcal/mol}$$
$$\Delta S^\circ = -0.5 \text{ eu}$$

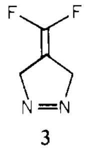
While the mechanism for the above rearrangement is generally conceded to involve trimethylenemethane (TMM) diradicals, neither the thermodynamic nor the accompanying kinetic data give *any* insight into the structure or the kinetic fate of such diradicals. Moreover, while "orthogonal" TMM's have been logically, and most likely correctly, implicated in a number of such rearrangements[6] and "planar" TMM's have been demonstrated to be "kinetically accessible" in others,[7,8] there is still no direct *experimental* evidence for the ground-state structure of singlet TMM's which have no steric impediment to planarity.

Table I. Product Ratios for Thermolysis and Photolysis of 4-(Difluoromethylene)-1-pyrazoline (3)

conditions	1	2	allene
162 °C, 5 mm, 15 min[a]	54.2	45.8	
162 °C, 700 mm, 15 min[b]	54.4	45.6	
150 °C, soln, 30 min	59.7	40.3	
$h\nu$, 2 mm, 30 min[c]	30.1	31.6	38.3
$h\nu$, 660 mm, 30 min[b]	56.6	42.2	1.2
$h\nu$, soln, 60 min	61.6	38.4	
equilibrium values, 193 °C[d]	14.2	85.8	

[a] Good first-order kinetics observed. [b] Argon added. [c] All photolyses at 38 °C and 3500 Å. [d] Reference 1.

It was our expectation that *some* significant insight into the nature of such TMM's might be gained by examining the *kinetic* behavior of those fluorine-substituted TMM's which could be generated by thermal or photochemical deazetation of pyrazolines **3** and **4**, which could be synthesized by diazomethane cycloaddition to 1,1-difluoroallene and fluoroallene, respectively.[9]



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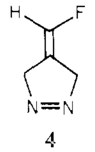

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While there is not universal agreement on the mechanism for deazetation of such pyrazolines,[6,10] it is generally accepted that *photochemical* deazetation does produce a trimethylenemethane species. The most direct evidence for this is the spectroscopic

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