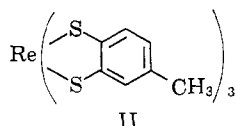


tensor.¹⁵ The lowest band maxima in the solution absorption spectrum of I in CHCl_3 occur at 8230 cm^{-1} (ϵ 1090), 14,050 (24,000), and 23,450 (12,300). In a solid sample the lowest maxima are at 8000, 13,500, and 23,000 cm^{-1} (± 200 cm^{-1}). The e.s.r. and electronic spectra clearly show that I retains the trigonal-prismatic structure in solution.

The polarographic behavior of I is very interesting. The complex exhibits three reversible reduction waves and one reversible oxidation wave in DMF solution, indicating the existence of the five different complexes $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3^n$ with $n = -3, -2, -1, 0,$ and $+1$. The half-wave potentials are $+0.163$ ($+1 \rightarrow 0$), -0.340 ($0 \rightarrow -1$), -1.812 ($-1 \rightarrow -2$), and -2.591 v. ($-2 \rightarrow -3$).¹⁶ The existence of several states simply related by one-electron transfer reactions is a characteristic of the $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_3^n$ systems.^{6,12}

To facilitate the investigation of the occurrence of trigonal-prismatic coordination, we have prepared a series of $\text{M}(\text{tdt})_3^n$ complexes with $\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Re}$ and $n = 0, -1$. Direct comparison with I is obtained with $\text{Re}(\text{tdt})_3$ (II). Complex II, prepared by



the reaction of ReCl_5 and toluene-3,4-dithiol in CCl_4 , is green and shows a single broad e.s.r. line (width, 100 gauss) at $g = 2.010 \pm 0.003$ in CHCl_3 or THF and a similar single line in a polycrystalline solid at $g = 2.010 \pm 0.003$ (width, 70 gauss). The polarographic behavior of II is quite similar to that of I, with half-wave potentials at $+0.387$ ($+1 \rightarrow 0$), -0.065 ($0 \rightarrow -1$), -1.577 ($-1 \rightarrow -2$), and -2.375 v. ($-2 \rightarrow -3$),¹⁶ indicating the existence of the corresponding five species of the type $\text{Re}(\text{tdt})_3^n$. The lowest band maxima in the electronic spectrum of II in CHCl_3 are at 7920 cm^{-1} (ϵ 300), 9220 (500), 14,450 (16,000), and 24,930 (11,000). In addition, II shows precisely the pattern of I in its e.s.r. spectrum at 77°K. in a DMF- CHCl_3 glass (although the hyperfine splittings are slightly larger).¹⁵ We conclude that complex II has a trigonal-prismatic array of donor atoms and that the ReS_6 fragment plays a dominant role in determining the electronic structure of both I and II.

We can now compare the results for I and II with the electronically similar complexes ML_3^- [$\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L} = \text{tdt}, \text{S}_2\text{C}_2\text{Ph}_2,$ ⁶ $\text{S}_2\text{C}_2(\text{CF}_3)_2$ ¹²] and VL_3^{2-} ¹³ ($\text{L} = \text{tdt}, \text{bdt}, \text{S}_2\text{C}_2\text{Ph}_2,$ and mnt). These complexes all have $S = 1/2$ and their e.s.r. spectra yield g values in a narrow range near 2.00. The relatively small (or absence of) anisotropy in the g tensor in the complexes measured to date cannot be adequately accommodated assuming merely a distorted octahedral structure.^{12,13} Comparing nonisoelectronic complexes, X-ray powder patterns show that $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$ and $\text{W}(\text{S}_2\text{C}_2\text{Ph}_2)_3$ are isomorphous and thus most probably isostructural.¹⁷ Furthermore, the infrared spectra of the $\text{M}(\text{tdt})_3$

(15) Full details of the e.s.r. and other results, and a more complete interpretation, will be presented in a subsequent paper.

(16) Potentials in volts measured in DMF using a d.m.e. with Ag-AgClO_4 reference electrode. Oscillopolarography was used to establish that all waves are reversible. We thank R. Williams for assistance.

(17) We thank R. Eisenberg for assistance.

($\text{M} = \text{Mo}, \text{W}, \text{Re}$) complexes are essentially identical. From the above results we conclude that many, if not all, of these six-coordinate complexes possess the unusual trigonal-prismatic geometry.¹⁸

The bidentate sulfur-donor ligands which form trigonal-prismatic complexes previously have been found to stabilize the square-planar configuration over a large number of central metal atoms and unusual electronic structures.¹⁹ It is likely that these same sulfur-donor ligands, in six-coordination, stabilize the trigonal-prismatic structure over an equally large series of metals and unusual electronic structures.

(18) It remains to be seen if the trigonal-prismatic geometry extends to such complexes as $\text{Cr}(\text{mnt})_3^{3-}$. This is formally a $\text{Cr}(\text{III}), d^3$ case, usually considered to be an excellent octahedral situation.

(19) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964), and references therein.

(20) National Science Foundation Predoctoral Fellow, 1965-1966.

(21) Alfred P. Sloan Research Fellow, 1964-1966.

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The Addition of Fluorenylidene to Olefins in the Presence of Hexafluorobenzene^{1,2}

Sir:

The majority of carbenes add to olefins to give cyclopropanes in which the stereochemical relationship of the groups attached to the double bond is maintained.^{3,4} Such additions are termed stereospecific. The reports^{5,6} that diphenylcarbene was not stereospecific in its reactions with olefins were accompanied by the explanation of Skell⁵ that triplet carbenes, typified by diphenylcarbene, would add to olefins in a nonstereospecific fashion. It has been wisely warned^{7,8} that all nonstereospecific additions need not be due to triplets and that all triplets need not add in a nonstereospecific manner. Nonetheless, the use of the stereochemical outcome of the additions of carbenes to olefins as a diagnostic for spin states has been persistent and widespread.^{3,4,9}

While reports of triplets are rare, the few examples available bear out Skell's explanation. Triplet methylene has been made by collisional deactivation of the

(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research (P.R.F. No. 265G).

(2) Portions of this work are taken from the thesis of K. R. Rettig submitted in partial fulfillment of the requirements for the A.B. degree at Princeton University.

(3) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(4) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

(5) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

(6) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

(7) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 119 (1964).

(8) P. P. Gaspar and G. S. Hammond, ref. 3, p. 235 ff.

(9) (a) H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4997 (1961); (b) W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *ibid.*, **85**, 2754 (1963); (c) E. Funakubo, I. Moritani, T. Nagai, S. Nishida, and S. Murahashi, *Tetrahedron Letters*, 1069 (1963); (d) R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 758 (1965); (e) P. S. Skell and R. R. Engel, *ibid.*, **87**, 1135 (1965); (f) L. D. Wescott and P. S. Skell, *ibid.*, **87**, 1721 (1965); (g) D. C. Blomstrom, K. Herbig, and H. E. Simmons, *J. Org. Chem.*, **30**, 959 (1965).

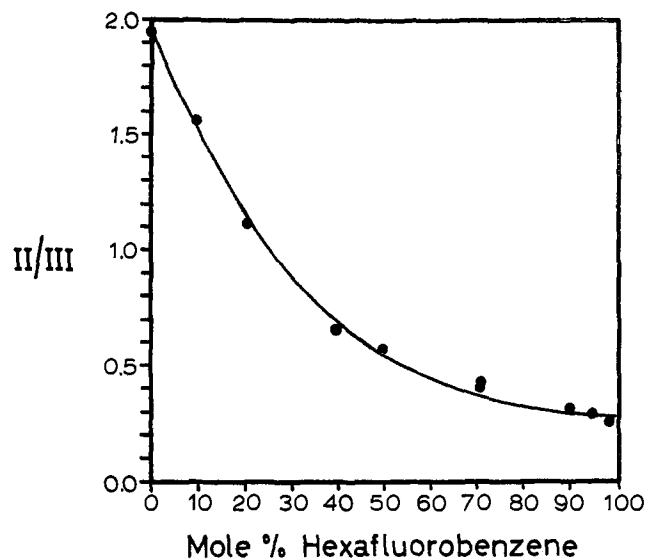


Figure 1. Irradiation of 9-diazofluorene in *cis*-2-butene and hexafluorobenzene.

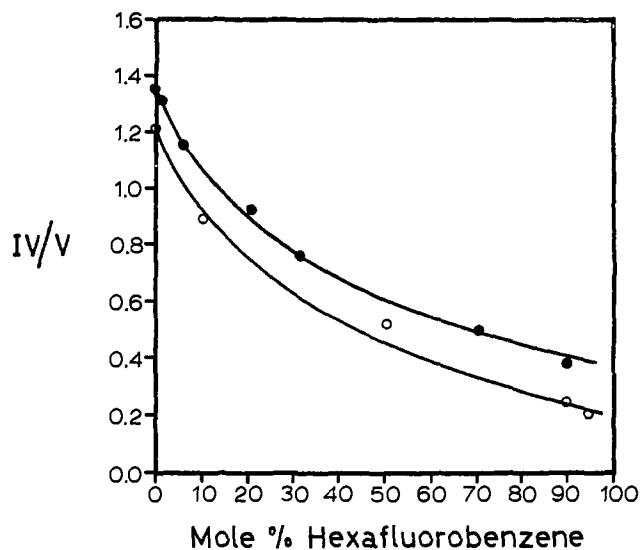
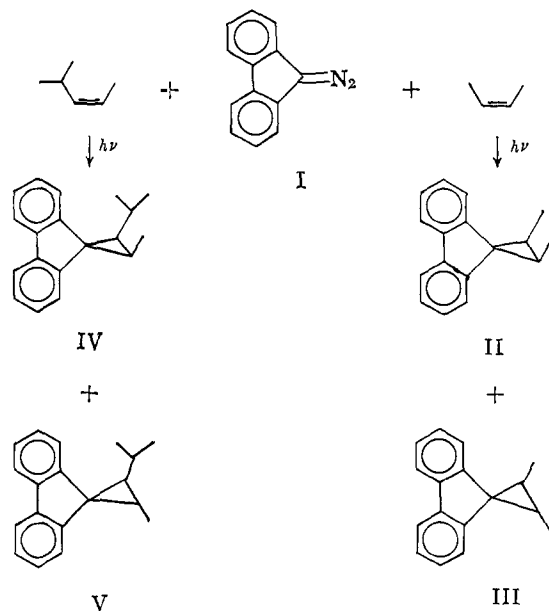


Figure 2. Irradiation of 9-diazofluorene in *cis*-4-methyl-2-pentene and hexafluorobenzene. Open circles, runs in nitrogen atmosphere; filled circles, runs in air.

singlet induced by inert molecules¹⁰⁻¹² and by processes of photosensitization.^{13,14} Triplet methylene made in these ways adds nonstereospecifically to olefins. Skell¹⁵ has recently shown that carbon in its ³P ground state is also nonstereospecific in its reactions with olefins.

We wish to report the generation of triplet fluorenylidene in solution by collisional deactivation of singlet fluorenylidene by hexafluorobenzene. The choice of hexafluorobenzene is dictated by the inertness of the carbon-fluorine bond toward carbenes¹⁵ and of the aromatic double bond toward fluorenylidene. Triplet



- (10) H. M. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960).
 (11) F. A. L. Anet, R. F. W. Bader, and A.-M. Van der Auwera, *ibid.*, **82**, 3217 (1960).
 (12) R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 1631 (1965). This paper appeared after the original submission of these communications and provides especially compelling evidence for singlet \rightarrow triplet conversion.
 (13) F. J. Duncan and R. J. Cvetanović, *J. Am. Chem. Soc.*, **84**, 3593 (1962).
 (14) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **84**, 1015 (1962).
 (15) G. G. Moore, Ph.D. Dissertation, Yale University, 1961.

fluorenylidene does indeed add nonstereospecifically to olefins, thus lending support to the hypothesis that all triplets will do so. In the succeeding communication¹⁶ we report that singlet fluorenylidene is stereospecific in its reactions with olefins.

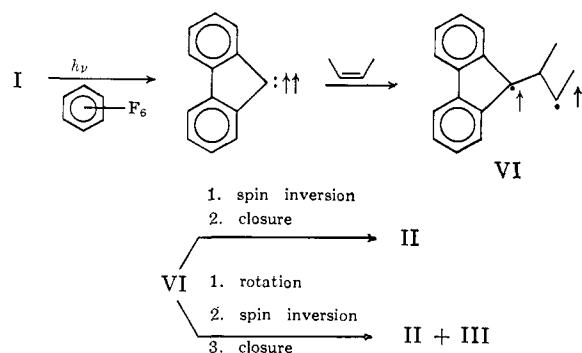
Irradiation of a solution of 9-diazofluorene (I) in *cis*-2-butene yields *cis*- and *trans*-2,3-dimethylspiro[cyclopropane-1,9'-fluorene]¹⁷ (II, III) in the ratio 1.95. Irradiation in *trans*-2-butene gives the same two products in the ratio 0.06. Similarly, irradiation of I in *cis*-4-methyl-2-pentene gives *cis*- and *trans*-2-methyl-3-isopropylspiro[cyclopropane-1,9'-fluorene] (IV, V) in the ratio 1.21. Irradiation in *trans*-4-methyl-2-pentene gives V and only traces of IV. The cyclopropanes are formed in ca. 50% yield and constitute 80-90% of the addition products. All irradiations were carried out in Pyrex vessels using General Electric sunlamps. Compounds IV and V were characterized by elemental analysis and their infrared and nuclear magnetic resonance spectra.

Assignment of stereochemistry is made on the following bases: Photolysis of I in *trans*-4-methyl-2-pentene would be expected to yield V as the major product and it is V which is the thermodynamically more stable isomer. Moreover, IV is the single cyclopropane formed by the cuprous chloride catalyzed decomposition of 9-diazofluorene in *cis*-4-methyl-2-pentene. This synthesis of cyclopropanes has been shown to be stereospecific.¹⁸

Addition of hexafluorobenzene to the irradiation mixtures results in increased yields of the *trans*-cyclopropanes. This is presumably a result of increased intersystem crossing from singlet fluorenylidene to the more stable triplet.¹⁹ The function of hexafluorobenzene is to allow nonreactive collisions of fluorenylidene. The reaction is completed by addition of trip-

- (16) M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4015 (1965).
 (17) W. von E. Doering and M. Jones, Jr., *Tetrahedron Letters*, 791 (1963).
 (18) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).
 (19) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).

let fluorenylidene to olefin followed by either spin inversion and closure or rotation, spin inversion, and closure. As long as the rate of rotation is of com-



parable magnitude to the rate of spin inversion and closure, the addition will be nonstereospecific.

It has been noted that II and III are interconverted when subjected to ultraviolet irradiation.¹⁷ We have found that this is also true for IV and V but have excluded photoisomerization as a possible source of apparent nonstereospecific addition. Mixtures of pure II and III and IV and V are recovered unchanged after being subjected to irradiation in cyclohexane containing small amounts of I. Apparently I and a side product of the reaction, 9,9'-bifluorenylidene, act as efficient filters of incident light. There is no isomerization of the olefins in the presence or absence of hexafluorobenzene.

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 Received June 10, 1965

Some Properties of Triplet Fluorenylidene. Detection of the Singlet State^{1,2}

Sir:

The preceding communication³ describes the nonstereospecific addition of fluorenylidene to olefins in the presence of hexafluorobenzene. We wish to consider here the mechanism proposed and to report some properties of singlet and triplet fluorenylidene.

The observed increase in nonstereospecific addition to either *cis*-4-methyl-2-pentene or *cis*-2-butene as hexafluorobenzene is added to the system is consistent with a mechanism invoking the intermediacy of triplet fluorenylidene. As pointed out previously³ nonstereospecific addition demands that the rate of rotation of the diradical VI⁴ be of comparable magnitude to the rate of spin inversion and closure to cyclopropanes. Similar mechanisms have been proposed in the past to account for other nonstereospecific additions of carbenes to olefins.^{5a-e}

(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research (P.R.F. No. 265G).

(2) Portions of this work are taken from the thesis of K. R. Rettig submitted in partial fulfillment of the requirements for the A.B. degree at Princeton University.

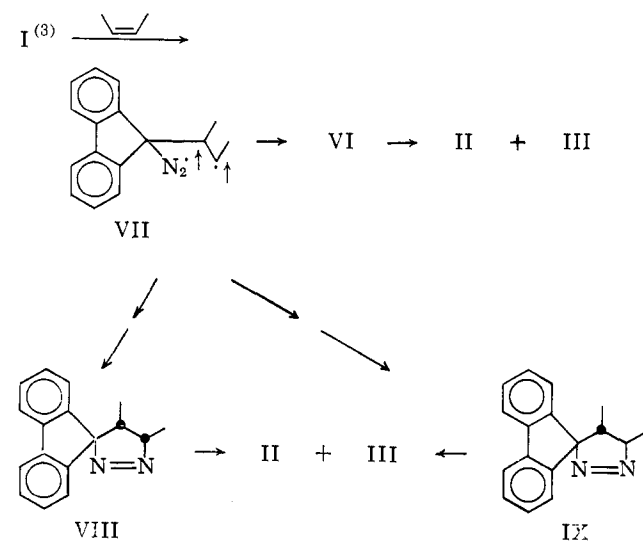
(3) M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4013 (1965).

(4) Formula numbers refer to those in the preceding communication.

(5) (a) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959); (b) F. J. Duncan and R. J. Cvetanović, *ibid.*,

As has been pointed out by DeMore and Benson⁶ and Gaspar and Hammond⁷ other mechanisms must be considered. Benson has proposed that all nonstereospecific additions can be explained by the intervention of less reactive, more selective carbenes. For a more selective carbene to be less stereospecific in its reactions with olefins requires that the barrier to rotation of diradical VI be lower than the barrier to closure. Several experiments clearly demonstrate, that, at least in solution, spin inversion and closure is generally faster than rotation. Hammond^{5c} finds at most a trace of *cis*-1,2-dimethylcyclopropane from the addition of triplet methylene to *trans*-2-butene. Even from *cis*-2-butene only one-third of the cyclopropane produced has the methyl groups *trans*. Similarly, diphenylcarbene gives less than 4% *cis*-1,1-diphenyl-2,3-dimethylcyclopropane from *trans*-2-butene and only ca. 13% *trans*-1,1-diphenyl-2,3-dimethylcyclopropane from *cis*-2-butene.⁸ Our results with fluorenylidene are similar. Fluorenylidene would be expected to be least energetic when large amounts of fluorocarbon have been added to the system. Under these conditions *trans*-2-butene gives only 12% of the *cis* adduct II. Rotation appears to be slow with respect to closure. The *cis* olefins do give products which have undergone substantial rotation. This could be explained on either an energy basis⁶ or by the reactions of triplets, while the data in the *trans* cases seem more compatible with a mechanism proceeding through triplets.⁹ Accordingly, we feel that our results do reflect the properties of triplet fluorenylidene and are not due to a lowering of the energy of the carbene.

The possibility that some or even all of the nonstereospecific additions observed are results of triplet I must be considered. Although there is recent evidence



84, 3593 (1962); (c) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **84**, 1015 (1962); (d) E. Funakubo, T. Moritani, T. Nagai, S. Nishida, and S. Murahashi, *Tetrahedron Letters*, 1069 (1963); (e) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).

(6) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

(7) P. P. Gaspar and G. S. Hammond in W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p. 235 ff.

(8) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

(9) A referee has pointed out that Benson's "hotness" is mostly vibrational excitation and should be lost very rapidly in solution.¹⁰

(10) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964).