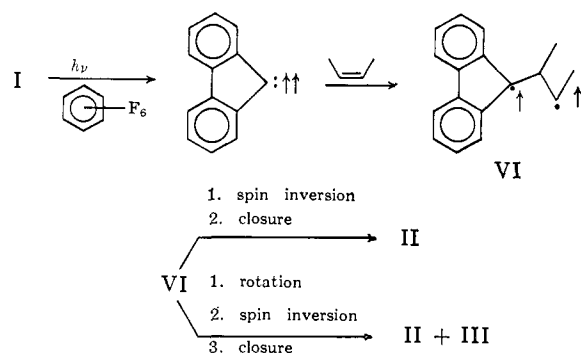


let fluorenylidene to olefin followed by either spin inversion and closure or rotation, spin inversion, and closure. As long as the rate of rotation is of com-



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.

Maitland Jones, Jr., Kenneth R. Rettig
Department of Chemistry, Princeton University
Princeton, New Jersey
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.

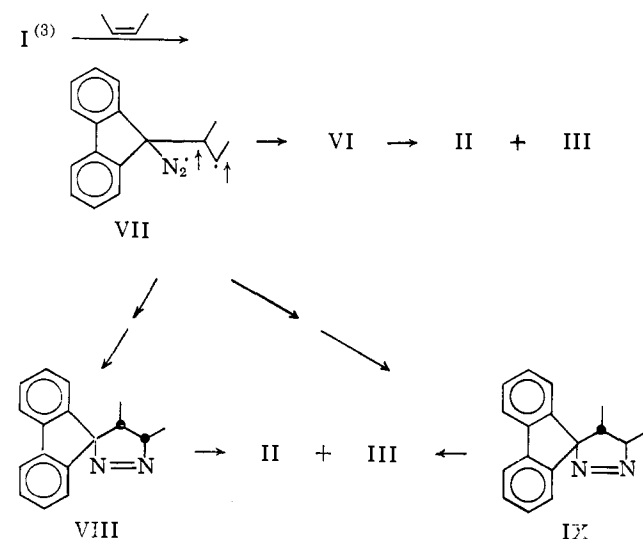
(3) M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4013 (1965).

(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"⁶ 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).

that some carbene precursors may undergo intersystem crossing before decomposition to carbenes,^{11,12} the possible importance of reactions of such triplets seems to have been largely ignored. Triplet I might add to an olefin to give a diradical intermediate VII. If the rate of loss of nitrogen from VII were greater than the rate of closure, the resulting diradical VI would be the same as postulated in our triplet carbene mechanism. Alternatively VII may close to give a pyrazoline faster than it loses nitrogen. Although such pyrazolines are known to decompose upon irradiation in a stereospecific fashion,¹³ we cannot finally reject a process in which rotation occurs in VII at a rate faster than closure to VIII and IX. These two pyrazolines could then decompose to give over-all nonstereospecific addition.

Irradiation of I in mixtures of *cis*-2-butene and 1,3-butadiene gives II, III, and the product of addition to the diene, 2-vinylspiro[cyclopropane-1,9'-fluorene] (X).

Table I

Hexafluorobenzene ^a	1,3-Butadiene ^a	<i>cis</i> -2-Butene ^a	II/III	(II + III)/X
0	0.0	10.0	2.1	
0	3.0	6.0	10.1	0.9
0	11.5	3.0	49 ^b	0.15
2	2.7	5.3	6.3	0.5
9	0.33	0.67	0.7	0.2
9	0.0	1.0	0.3	

^a mmols. ^b Difficulties in analysis make this number less reliable than the others. It is probably good to within 10%.

Added 1,3-butadiene causes the reaction with *cis*-2-butene to become more stereospecific. As more 1,3-butadiene is added, the ratio of *cis*-cyclopropane to *trans*-cyclopropane (II/III) increases and the ratio of butene adducts to diene adducts [(II + III)/X] decreases. A species capable of nonstereospecific addition is being removed, leaving a species which adds to the butene stereospecifically or very nearly so. Triplet fluorenylidene is being scavenged by the butadiene, leaving behind the singlet. It seems reasonable that a species adding to give a diradical would be better able to take advantage of allylic resonance than a species adding in a one-step process to give cyclopropane directly. Diphenylcarbene is reported to prefer 1,3-butadiene and 1,1-diphenylethylene to unconjugated olefins by a factor greater than 100.^{5a} The ratio of II to III drops again when hexafluorobenzene is added to the system. As more triplets are formed more of them will add to the *cis*-2-butene even in the presence of butadiene. Therefore, at a constant ratio of *cis*-2-butene to 1,3-butadiene, added hexafluorobenzene should decrease II/III, as is observed.

Oxygen has an effect similar to that of 1,3-butadiene. When the irradiations are run not under nitrogen but in air, the plots of *cis/trans* vs. mole per cent hexafluorobenzene are displaced to higher values (see Figure

(11) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964).

(12) S. Ho, I. Unger, and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **87**, 2297 (1965).

(13) T. V. Van Auken and K. L. Rinehart, Jr., *ibid.*, **84**, 3736 (1962).

2 in ref. 3). This is consistent with a scavenging of triplets by oxygen leaving behind a population of fluorenylidene richer in the singlet.

Thus we are able to observe two distinct species of fluorenylidene. The triplet state adds nonstereospecifically to olefins, prefers dienes to unconjugated olefins, and reacts faster with oxygen, while the singlet is stereospecific¹⁴ in its reactions with olefins.

(14) See Table I, footnote b.

Maitland Jones, Jr., Kenneth R. Rettig

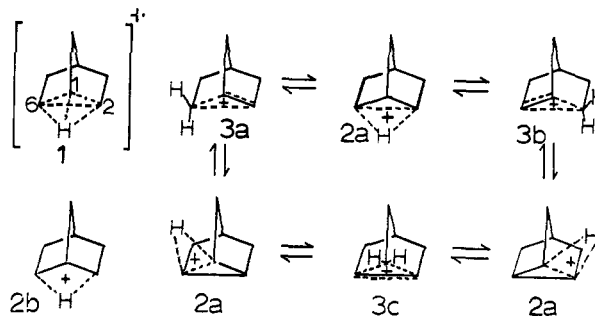
Department of Chemistry, Princeton University
Princeton, New Jersey

Received June 10, 1965

The Absence of Nortricyclonium Species in a Norbornyl Cation System. The Stereochemistry of 6,2-Hydride Shifts¹

Sir:

Transannular ("6,2") hydride shifts^{2,3} in norbornyl cations have been formulated with "nortricyclonium" ions (1)^{3a,b} (face-protonated cyclopropanes, which in the unsubstituted case are threefold symmetric^{3c}) and alternatively^{4,5} with edge-protonated cyclopropane species 2a as intermediates from which products are formed or as transition states through which nonclassical norbornyl cations (3) are interconverted.



The essential difference between 1 and 2a lies in symmetry properties. Thus, in the collapse of 1 to 3a, 3b, 3c, or product, the hydrogen that lies on the threefold axis cannot show any preference for attachment to either side of any of the carbon atoms (C-1, C-2, and C-6) surrounding the axis. In other words, the *endo-exo* distinction at the terminus (or, by microscopic reversibility, the origin) of hydrogen migration is lost in 1. Such is not the case in 2a or any similar edge-protonated species. This difference provides in principle the basis of an experimental distinction between the nortricyclonium ion 1 and other conceivable species, including but not limited to 2a. (For example, species 2b could be imagined to differ from 2a in C-2-C-6 distance and would not be desig-

(1) The support of part of this work by the National Science Foundation and by the National Institute of Arthritis and Metabolic Diseases through Grant No. AM-07505 is gratefully acknowledged.

(2) W. von E. Doering and A. P. Wolf, XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., 1951, Abstracts, p. 437; *Perfumery Essent. Oil Record*, **42**, 414 (1951).

(3) (a) J. D. Roberts and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 5009 (1951); (b) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954); (c) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956), discuss hydride shift in 7-chloronorbornyl cation.

(4) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952).

(5) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965).