

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.

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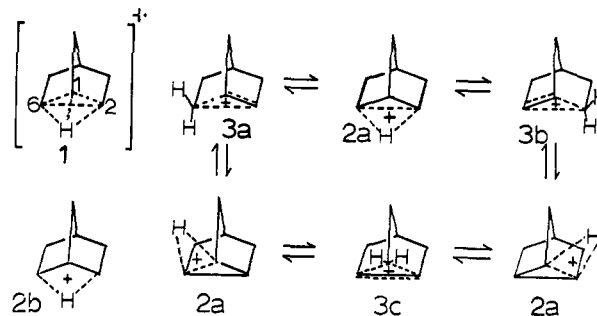
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The Absence of Nortricyclonium Species in a Norbornyl Cation System. The Stereochemistry of 6,2-Hydride Shifts¹

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).

nated as a "protonated cyclopropane"). By way of 1 or a properly substituted derivative, an *endo*-hydrogen at C-6 will migrate to the two possible configurations at C-2 with exactly or approximately equal probability, whereas in **2a**, **2b**, or related species it will migrate exclusively to become bound *endo* to C-2. We now report experiments which show that, in the 2-carboxy-3-methyl-5-norbornyl cation, intramolecular transannular hydride shift is exclusively *endo* → *endo*.

trans-Crotonic acid-3-*d*, prepared⁶ from acetaldehyde-1-*d*⁷ and malonic acid, reacts with cyclopentadiene to give a mixture of 3-*exo*-methyl-5-norbornene-2-*endo*-carboxylic acid-3-*endo-d* (**4b**) and 3-*endo*-methyl-5-norbornene-2-*exo*-carboxylic acid-3-*exo-d* (**5b**), which can be separated by the iodolactone method, as in the undeuterated series **4a** and **5a**.⁸ The position of the deuterium in **4b** and **5b** is evident from the method of synthesis, from the collapse of the n.m.r. methyl doublets of **4a** and **5a** to singlets, and from the disappearance of the one-proton multiplets of the C-3 hydrogen of **4a** and **5a** in the spectra of **4b** and **5b**.

Under conditions (50% by volume sulfuric acid, 21 hr.) previously reported⁸ to give the lactones **6a** and **7a** from either **4a** or **5a**, either deuterated acid **4b** or **5b** gives the unrearranged lactone **6b** (that from **4b** being isolated in quantity sufficient to show that deuterium is exclusively at C-3) and the rearranged lactone **7b**, with deuterium exclusively at C-2.

The total deuterium content of products **6b** and **7b** is the same as that of the starting materials, and, accordingly, the deuterium shift, which on purely structural grounds must have occurred, is entirely intramolecular. The complete disappearance in the n.m.r. spectrum of **7b** of the one-proton signal at 4.18 p.p.m. (downfield from tetramethylsilane), which is associated with the C-2 hydrogen of **7a**, indicates that less than about 3% of C-2 protio species can be present. The results are in accord with the indicated mechanism (in which the question of nonclassical or classical nature of the cations is temporarily begged).⁹

The intermediates or transition states for the two hydride shifts required to transform **4b** to rearranged lactone **7** by way of nortricyclonium species would be represented as **10** and **11**. Formation of exclusively 2-deuterio lactone **7b** then becomes inexplicable; this product would arise from **11**, but **10**, which is formed *earlier* in the reaction scheme and differs from **11** only in that the positions of deuterium and the C-2 hydrogen are reversed, would have been expected to form 2-protio rearranged lactone, in conflict with experiment.¹⁰

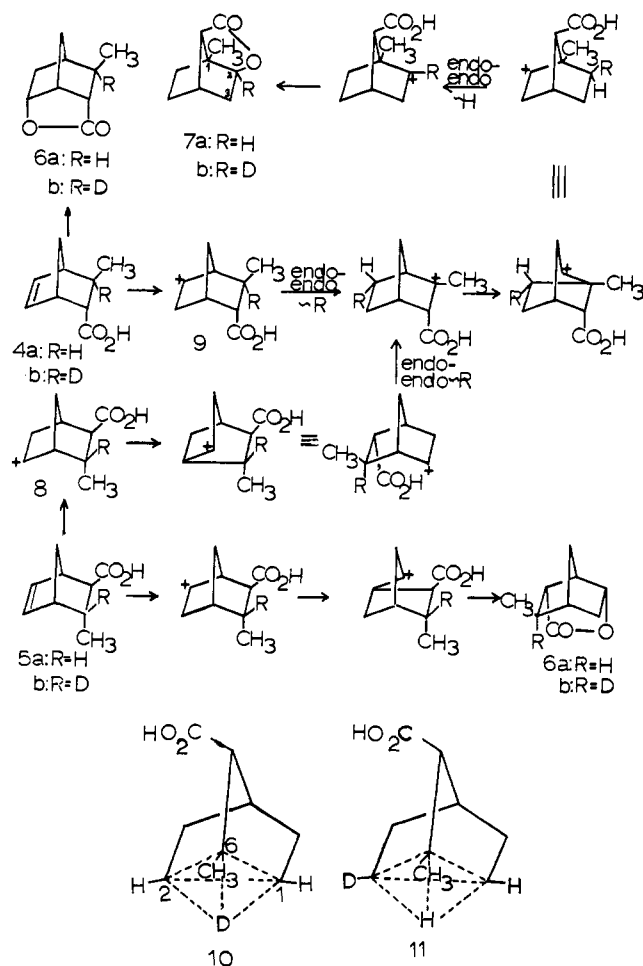
(6) K. von Auwers, *Ann.*, **432**, 46 (1923).

(7) L. C. Leitch, *Can. J. Chem.*, **33**, 400 (1955).

(8) S. Beckmann, H. Geiger, and M. Schaber-Kiechle, *Chem. Ber.*, **92**, 2419 (1959).

(9) Although **7b** could also be produced formally from **4b** or **5b** by successive exclusive *endo*-*exo* deuterium shift and *exo*-*endo* or *exo*-*exo* hydrogen shift, this mechanism seems highly unlikely since it requires mutually inconsistent and curiously perverse specificities in both steps. Furthermore, such specificity would not be a reasonable consequence of the nortricyclonium ion intermediate.

(10) (a) We recognize that the methyl group of **10** would perturb the threefold symmetry of the electron distribution characteristic of **1**, so that the C-1-C-6 and C-2-C-6 bonds would differ from the C-1-C-2 bond. This would have no effect on the point in question. Strictly speaking, even the twofold "symmetry" of **10** is only nominal, since the carboxyl group would introduce some small perturbation; it seems unlikely that this could be decisive.



We conclude that nortricyclonium ions with the symmetry properties of **10** are not involved in these rearrangements. The possibility that their threefold symmetric counterparts may be involved in the unsubstituted norbornyl case cannot yet be rigorously excluded, but grounds for expecting different behavior there must now be supplied.

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The Tripropynylcarbonium Ion. Charge Delocalization in Ethynyl- and Propynylcarbonium Ions

Sir:

We have greatly extended previous observations¹ of alkynyl cations to include the tripropynylcarbonium ion (**1**), ethynyl-substituted carbonium ions, and a greater variety of propynylcarbonium ions.

The n.m.r. spectrum³ of the tripropynylcarbonium ion (**1**) is shown in Figure 1. The spectrum of the ethynyl-

(1) Two propynylcarbonium ions were described recently.² The ultraviolet spectra of several 1,1,5,5-tetraarylpent-4-en-2-yl cations had been reported earlier [H. Fischer and H. Fischer, *Ber.*, **97**, 2959 (1964)]; we regret not having referred to this paper in ref. 2.

(2) H. G. Richey, Jr., J. C. Phillips, and L. E. Rennick, *J. Am. Chem. Soc.*, **87**, 1381 (1965).

(3) Chemical shifts are expressed in p.p.m. relative to tetramethylsilane as 10.00. Tetramethylammonium chloride, used as an internal reference, was assumed to absorb at 6.90.