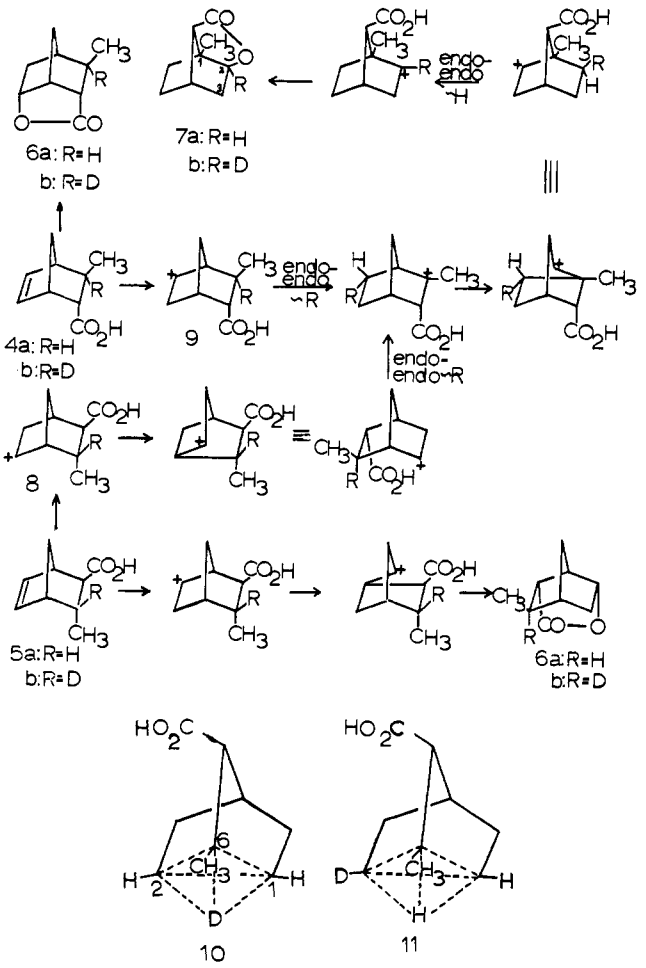
nated as a "protonated cyclopropane"). By way of **1** or a properly substituted derivative, an *endo*-hydrogen at C-6 will migrate to the two possible configurations at C-2 with exactly or approximately equal probability, whereas in **2a**, **2b**, or related species it will migrate exclusively to become 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*, prepared[6] 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 reported[8] 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]



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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(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.

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

Sir:

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

The n.m.r. spectrum[3] 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. Philips, 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.

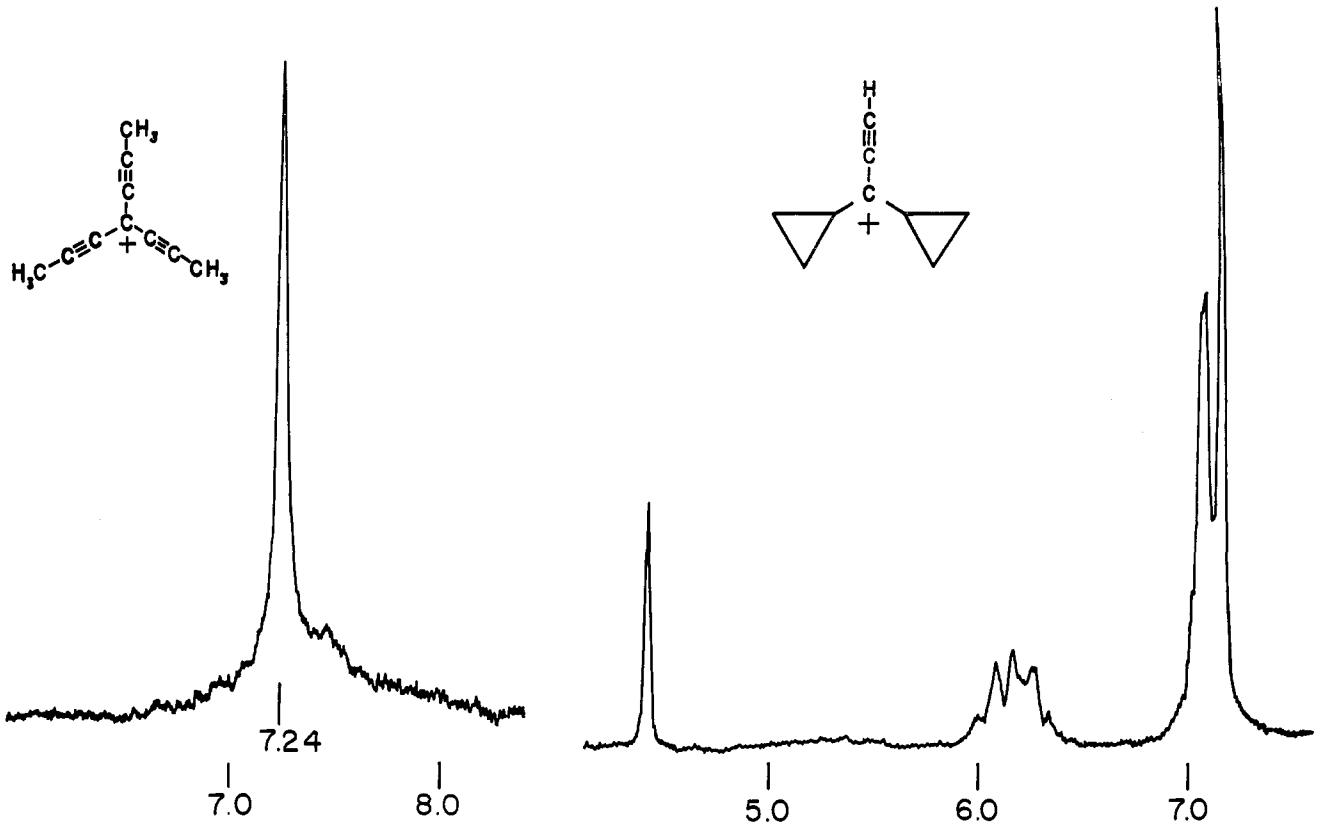
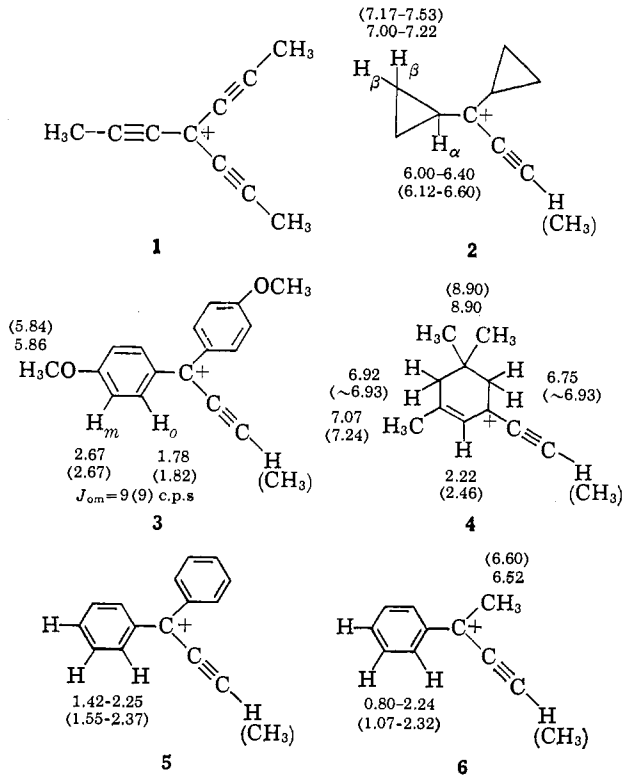


Figure 1. N.m.r. spectra of fluorosulfonic acid solutions of the tripropynyl- and ethynyldicyclopropylcarbonium ions at −60°.

dicyclopropylcarbonium ion (**2**) is given in Figure 1 as an example of the ethynylcarbonium ion spectra. The chemical shifts of ethynyl (C≡CH) and propynyl (C≡C—CH_3) hydrogens of the observed carbonium ions are tabulated in Table I. The positions of other absorptions in the n.m.r. spectra are indicated on structures **2**–**6** (the numbers in parentheses are for the propynyl ions; the other numbers are for the ethynyl ions).



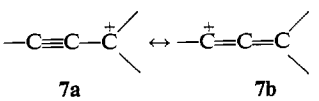
1 **2** **3** **4** **5** **6**

Table I. Positions of N.m.r. Absorptions of Ethynyl and Propynyl Hydrogens of the Carbonium Ions at −60°

	Ethynyl ions		Propynyl ions	
System	C≡CH in ion	C≡CH in ion minus its position in alc. precursor[a]	C≡C—CH_3 in ion	C≡C—CH_3 in ion minus its position in alc. precursor[a]
1			7.24	− .89
2	4.42	−3.35	7.57	− .63
3	4.30	−3.05	7.40	− .73
4	3.68	−4.00	7.37[b]	− .85[b]
5	3.04	−4.35	7.12	−1.06
6	2.76	−4.76	7.06	−1.12

[a] The alcohol spectra were of carbon tetrachloride solutions at room temperature. [b] The C≡C—CH_3 absorption may instead be at 7.24, in which case the shift from the alcohol would be −0.98.

The absorptions of the propynyl hydrogens in the ions are downfield from the similar absorptions of the alcohol precursors of the ions by ~0.8 p.p.m. as reported previously.[2] The absorptions of the ethynyl hydrogens show much more dramatic downfield shifts. The magnitude of these shifts provides evidence that the carbon to which the ethynyl hydrogen is attached is involved significantly in charge delocalization as shown in resonance structure **7b**. Increasing down-



7a **7b**

field shifts of the ethynyl and propynyl hydrogen parallel roughly the order of decreasing carbonium ion stability for systems **3–6**. This systematic variation in chemical shift reflects increasing delocalization of positive charge into ethynyl and propynyl groups as the remainder of the system becomes less effective at delocalizing the charge.

The ethynyl- and propynyldicyclopropylcarbonium ions are anomalous. System **2** should be more stable than **5** or **6** but less stable than **3**,[4] yet the downfield shifts of the ethynyl and propynyl hydrogens are smaller than in the other ions. It is tempting to suggest that these ions may have increased stability due to interaction between the cyclopropyl rings and the triple bond.

The absorptions due to hydrogens other than C≡CH or C≡C—CH_3 of the ions also are downfield from the similar absorptions of the parent alcohols. The spectra resemble those reported for the corresponding ions with methyl instead of ethynyl and propynyl groups.[7,8] The absorptions of each propynyl ion were usually upfield from the absorptions of the corresponding ethynyl ion. This is consistent with the conclusion that C≡C—CH_3 accepts more of the positive charge than C≡CH and is another indication of the importance of charge delocalization into ethynyl and propynyl substituents.

Most of the carbonium ions were generated by addition of sulfur dioxide solutions[9] of the corresponding alcohols[10] to fluorosulfonic acid.[11] To prepare the tripropynyl- (**1**) and the phenylmethylcarbonium (**6**) ions, sulfur dioxide solutions of the alcohols were added to solutions of one volume of antimony pentafluoride in about three volumes of fluorosulfonic acid.[14] The solutions were mixed at −78° and n.m.r. spectra were taken at −60°.

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(15) Alfred P. Sloan Foundation Research Fellow.

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Bis(trifluoromethyl)ketene

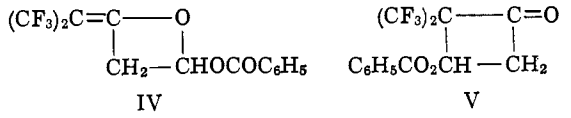
Sir:

Bis(trifluoromethyl)ketene (I), prepared in excellent yield by a simple process, is thermally very stable and has an extensive new chemistry. The synthesis[1] is accomplished by heating a mixture of hexafluoroisobutyric acid (II)[2] and excess phosphorus pentoxide (molar ratio *ca.* 1:2) up to 250° pot temperature at atmospheric pressure. The ketene is collected in over 90% yield in a −80° trap.

$$\underset{\text{II}}{(CF_3)_2CHCOOH} \xrightarrow{P_2O_5} \underset{\text{I}}{(CF_3)_2C{=}C{=}O} \overset{F^-}{\rightleftharpoons} \underset{\text{III}}{CF_2{=}C(CF_3)COF}$$

Bis(trifluoromethyl)ketene (I, b.p. 5°; 4.54 μ (C=C=O) infrared absorption) and perfluoromethacrylyl fluoride (III, b.p. 52°; 5.40 (C=O) and 5.80 μ (C=C) infrared absorptions) are in equilibrium in the vapor phase over anionic catalysts such as sodium fluoride.[3]

Bis(trifluoromethyl)ketene also reacts with uncharged nucleophiles. Illustrative is the formation of adducts with olefins with an ease roughly paralleling the nucleophilicity of the olefin. Cycloaddition to both the C=C and C=O groups of ketene I can occur as shown by formation of adducts IV (m.p. 99–100°; 5.72 (C=O) and 5.82 μ (C=C) infrared absorptions) and V (m.p. 45–46°; 5.50 (ketone) and 5.74 μ (ester carbonyl) infrared absorptions) with vinyl benzoate at 100°, formed in 34 and 42% yields, respectively.



IV V

Simple alkenes also add to ketene I to form cyclobutanones and linear adducts. A condensed phase is necessary, so lower alkenes require higher pressures. A mixture, b.p. 63–70° (100 mm.), obtained from propylene at 150° and 800 atm., was separated by gas chromatography into about 70% of a cyclobutanone (5.50 μ (C=O) infrared absorption) and 30% linear ketone VI (5.72 (C=O) and 6.15 μ (C=C) infrared absorptions). Ketene I gives the β-lactone VII (b.p. 95°; 5.35 μ (C=O) infrared absorption) with trioxane using zinc chloride as catalyst in ether at 150° and the

(4) The pK_{R^+} values for the triphenylmethyl-,[5] tricyclopropyl-,[6] and tri-*p*-methoxyphenylcarbonium[5] ions are −6.63, −2.31, and 0.82, respectively.

(5) N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3051 (1955).

(6) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, in press.

(7) G. A. Olah, *ibid.*, 86, 932 (1964); D. G. Farnum, *ibid.*, 86, 934 (1964); N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, 85, 2991 (1963); R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, 37, 1402 (1959).

(8) N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *J. Am. Chem. Soc.*, 87, 3000 (1965); C. U. Pittman, Jr., and G. A. Olah, *ibid.*, 87, 2998 (1965).

(9) Dichloromethane solutions of some of the alcohols also were added successfully to fluorosulfonic acid.

(10) The only alcohol not prepared previously, 1,1-dicyclopropyl-2-butyn-1-ol, was synthesized by addition of propynyllithium to dicyclopropyl ketone.

(11) Fluorosulfonic acid has been used as a medium for generating carbonium ions.[8,12,13]

(12) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, 42, 502 (1964); T. S. Sorensen, submitted for publication.

(13) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, 87, 2997 (1965).

(14) Fluorosulfonic acid–antimony pentafluoride solutions have been recommended for the preparation of carbonium ions.[13]

(1) We are grateful to Dr. S. Andreades of this laboratory for helpful discussions leading to this route. Bis(trifluoromethyl)ketene and its isomer, perfluoromethacrylyl fluoride, have also been prepared independently by less attractive routes by I. L. Knunyants *et al.*, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1265, 1432, (1963).

(2) I. L. Knunyants, L. German, and B. Dyatkin, *Bull. Acad. Sci. USSR Div. Chem. Sci.*, 1391 (1956).

(3) Anionic catalysis of fluoroolefin reactions is well documented. See, for example, W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *J. Am. Chem. Soc.*, 82, 3091 (1960).