possible to construct a solvent nucleophilicity scale applicable to a wide variety of molecules.

Acknowledgments. This work was supported by grants from the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, the National Institutes of Health (AI-07766), and the Smith, Kline and French Laboratories. P. v. R. S. thanks his hosts at the University of Michigan where background material for this set of papers was assembled. Professor S. Winstein provided critical comments.

[16] National Institutes of Health Postdoctoral Fellow, 1967–1969.

[17] American Can Company Fellow, 1966–1967; National Institutes of Health Predoctoral Fellow, 1967–1968; Ph.D. Thesis, Princeton University, 1970.

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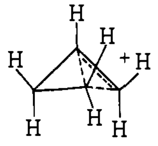
Received May 26, 1969

Stable Carbonium Ions. XCVIII.[1] The Nonclassical Cyclopropylcarbinyl Cation[2]

Sir:

The structure of the intermediate cation in cyclopropylcarbinyl–cyclobutyl solvolyses systems has been the subject of intensive study for many years.[3] Of the structures proposed, rapidly equilibrating unsymmetrical bicyclobutonium ions such as **1** have been most widely accepted.[3] The "bisected" structure **2** has also received support.[4] More recently a C_s symmetric ion, **5**,[5] has been suggested as the ion linking degenerate cyclopropylcarbinyl ions. The still more symmetrical (C_{3v}) tricyclobutonium ions **3** and **4** have been considered but were deemed unlikely on the basis of theoretical calculations.[5c,6]



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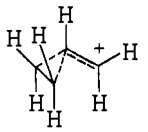

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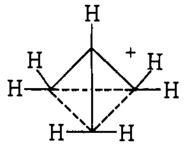

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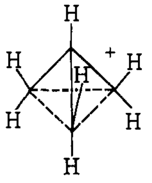

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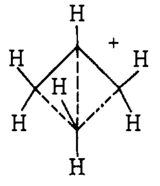

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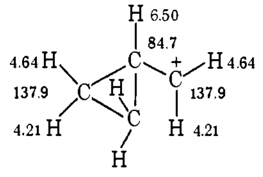
We now wish to present ^{1}H and ^{13}C nmr spectroscopic data on the directly observed, long-lived cyclopropylcarbinyl cation (**6**) which provide evidence for the nonclassical nature of this ion.

When cyclopropylcarbinol or cyclobutanol is dissolved in SbF_5–SO_2ClF at $-80°$,[7] a clear yellow-brown solution is obtained which exhibits an nmr spectrum (Figure 1) from which both ^{1}H and ^{13}C parameters can be obtained[8] (Table I). The one-proton methine multiplet at δ 6.50 is made up of two overlapping quartets with $J_1 = 8.0$, $J_2 = 6.5$ Hz, as shown by decoupling first the three-proton methylene doublet at δ 4.64 and subsequently the three-proton doublet at δ 4.21. When α,α-dideuteriocyclopropylcarbinol (prepared by $LiAlD_4$ reduction of cyclopropanecarboxylic acid) is ionized, the methine multiplet consists of a pair of nearly overlapping triplets, and the intensity of the methylene doublets is decreased by one-third.[9]

Using the indor technique,[10] the ^{13}C spectrum was obtained by monitoring each of the methylene doublets in turn. The spectra obtained were *identical*, giving for the methylene carbons $\delta(^{13}C)$ 137.9 ± 0.1 ppm (CS_2) and $J(^{13}CH) = 180 \pm 5$ Hz. The ^{13}C shift of the methine carbon, obtained by enhancement of the high-field proton doublet, was found to be 84.7 ppm. The conclusions drawn from the nmr spectra are that the methylene protons are nonequivalent and form two groups of equivalent protons coupled to carbons with the same chemical shift and coupling constant, *i.e.*, identical carbon atoms. The absence of geminal methylene hydrogen coupling is somewhat surprising, but it is not unreasonable since the value of J_{CH} (180 Hz) is consistent with sp^2 hybridization of the carbon atom, and J_{gem} is known to decrease to near zero in some cases.[11,12]

In order to compare the primary cyclopropylcarbinyl system (**6**) with secondary and tertiary alkylcyclo-



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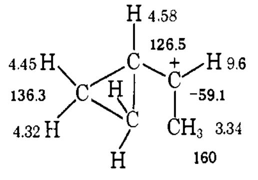

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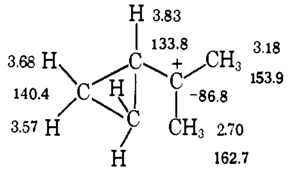

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[1] Part XCVII: G. A. Olah, D. P. Kelly, and N. Suciu, *J. Amer. Chem. Soc.*, in press.

[2] Presented in part at the 21st National Organic Chemistry Symposium, Salt Lake City, Utah, June 1969.

[3] The literature has been reviewed by K. B. Wiberg, A. H. Hess Jr., and A. J. Ashe III in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Editors, Vol. III, Wiley-Interscience, New York, N. Y., 1970, in press.

[4] P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966), and references therein.

[5] (a) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); (b) K. B. Wiberg and G. Szeimes, *J. Amer. Chem. Soc.*, **90**, 4195 (1968); (c) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303, 4311 (1968).

[6] M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, **No. 2**, 403 (1963).

[7] The alcohol is frozen onto the side of a test tube containing the acid solution at −78°, then gently washed into solution by a vortex mixer.

[8] A similar spectrum was obtained previously from cyclobutane, but the low-field multiplet (δ 6.5) was not well resolved: G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **90**, 933 (1968). See also C. H. Lin, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1969, in which the same ion was generated from cyclopropylcarbinyl and cyclobutyl chlorides.

[9] This experiment was carried out by J. M. Bollinger.

[10] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 2943 (1969).

[11] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, New York, N. Y., 1969, Chapters 1–4.

[12] Ion **6** was quenched in a suspension of methanol and sodium carbonate at −78°. The presence of cyclobutyl methyl ether and cyclopropylcarbinyl methyl ether is indicated (nmr) in the products obtained. Details will be reported in a forthcoming full paper.

Table I. Nmr Parameters of Cyclopropylcarbinyl Cations[a]

	$\delta(^1H)$ (J_{H-H})[b]				$\delta(^{13}C)$ (J_{CH})[c]			
	Alkyl		Cyclopropyl					
Ion	CH_3	$\overset{+}{C}H$	CH_2	CH	CH_3	CH_2	>CH	C^+
6			4.21 (6.5) 4.64 (8.0)	6.50 (6.5, 8.0)		137.9 (180)	84.7	
7	3.34 (6.2)	9.6 (6.2)	4.32 4.45	4.58	160	136.3	126.5	−59.1
8	2.70, 3.18 (1.25)		3.57 3.68	3.83	153.9 (125) 162.7 (125)	140.4	133.8	−86.8

[a] Determined on an HA-100 instrument at −70° in SbF_5–SO_2ClF solution. [b] Parts per million from external TMS, J in hertz. [c] Parts per million from CS_2, determined by the indor method.

propylcarbinyl cations, we have also obtained the complete ^1H and ^{13}C spectra of the methylcyclopropyl- and dimethylcyclopropylcarbonium ions (**7** and **8**), respectively. ^1H and ^{13}C nmr data are summarized in Table I. Chemical shifts of ions **6**–**8** are also shown on the structures (^{13}C shifts are displayed in boldface type).

Ion **8** has been investigated previously,[13,14] but additional and improved data have now been obtained, showing fine structure of the methyl signals due to allylic coupling through the carbonium ion center. The ^{13}C shifts of **8** indicate delocalization of part of the charge onto the cyclopropane ring ($\delta(^{13}C^+)$ of **8** −86.8 (*cf.* $\delta(^{13}C^+)$ of $(CH_3)_3C^+$ −135.4 ppm),[14] $\delta(^{13}CH_2)$ of **8** 140.4 (*cf.* $\delta(^{13}C)$ of c-C_3H_6 196.3)).[15]

Replacement of a methyl group by hydrogen, which is known to produce only relatively small changes (about 10 ppm to higher field) in the ^{13}C shift of both carbonium ions[14] and neutral compounds,[16–18] results in a marked shielding of the carbonium ion carbon of **7**. This is no doubt due to an increase in σ delocalization in the secondary ion **7** (*cf.* the tertiary ion **8**), and can be envisaged as a "drawing-in" of the positive center toward the cyclopropane ring to give a more symmetrical structure for **7** than for **8** obviously the more symmetric the species (*i.e.*, approaching C_{3v} symmetry) the higher the value of J_{CH} for the cyclopropyl methine proton.[19] The proton spectrum of **7** shows the ^+C–H proton multiplet at δ 9.6, made up of a doublet of quartets (J_1, J_2 = 6.2 Hz) which collapses to a doublet (J = 6.2 Hz) on irradiation of the methyl doublet at δ 3.34. The cyclopropyl protons appear as a multiplet centered at δ 4.5.

Equilibrating classical cyclopropylcarbinyl cations[20] would result in the averaging of the methylene ^{13}C shifts and that of the carbonium ion center. From the ^{13}C data of ions **7** and **8**, one might expect a $\delta(^{13}C^+)$ of *ca.* −30 ppm for a static primary ion. Using this value and the observed average ^{13}C shift of the methylene carbons in the cyclopropylcarbinyl cation (137.9 ppm), one obtains a calculated value of 222 ppm for the cyclopropyl methylene carbons in **6**.[21] This value is obviously unacceptable, not only when compared with the related values in **7** and **8** but also when compared with the value of cyclopropane itself.[15] Consequently the ^{13}C data exclude an equilibrating "classical" cyclopropylcarbinyl ion. Of the nonclassical structures proposed, the tricyclobutonium ion (**4**) first suggested by Roberts and Mazur[22] would fit the spectroscopic data. However, subsequent work by Roberts shows incomplete scrambling among the methylene groups in solvolysis reactions.[23] Furthermore as previously mentioned, structures **4** and **5** are unattractive on theoretical grounds.[5c,6] The present experimental data can be best accommodated by rapidly equilibrating nonclassical cations **1** or **2** through a puckered cyclobutyl type ion **5**, the lifetime of which is too short to allow the methylene protons to become equivalent.

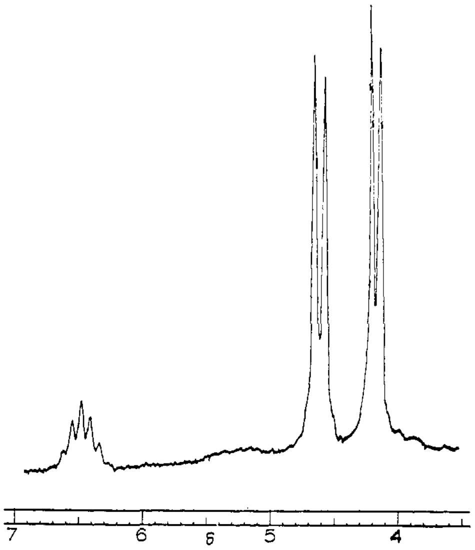

Figure 1. Pmr spectrum of the cylopropylcarbinyl cation **6** in SbF_5–SO_2ClF solution at −80°.

While the data presented do not enable a distinction to be made between equilibrating nonclassical bicyclobutonium or bisected cyclopropylcarbinyl ions, they do provide a clear distinction between σ-delocalized (nonclassical) structures and equilibrating classical ions. The data show a dramatic increase in the σ delocalization in the order dimethylcyclopropyl (**8**) <

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(13) (a) C. U. Pittman, Jr., and G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 2998 (1965); (b) *ibid.*, **87**, 5123 (1965).

(14) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

(15) J. J. Burke and P. C. Lauterbur, *ibid.*, **86**, 1870 (1964).

(16) B. V. Cheney and D. M. Grant, *ibid.*, **89**, 5319 (1967).

(17) D. M. Grant and E. G. Paul, *ibid.*, **86**, 2984 (1964).

(18) L. M. Jackman and D. P. Kelly, *J. Chem. Soc., B*, in press.

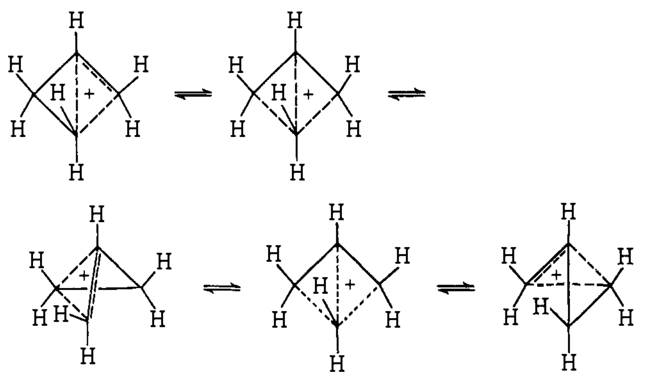
(19) From the available literature (see K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 185 (1968), this should be ~200 Hz for the C_{3v} tricyclobutonium ion. The low intensity of the methine proton absorption in the cyclopropylcarbinyl cation has so far prevented us from obtaining this value experimentally.

(20) H. C. Brown, *Spec. Publ. Chem. Soc.*, No. **16**, 2 (1962).

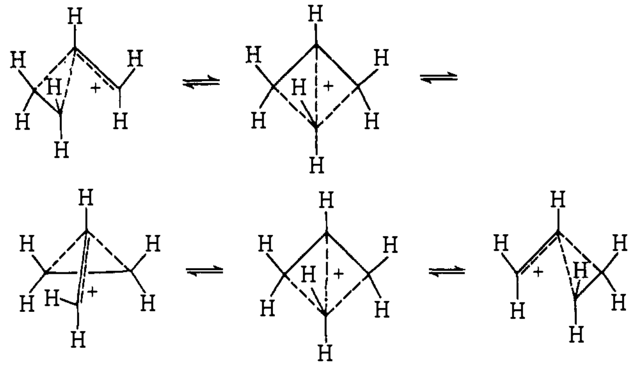
(21) If a value as low as 0 is assumed for the ^{13}C shift of the carbonium ion center in **6**, the value calculated for the ^{13}C shift of the cyclopropyl methylene carbons is 206 ppm, and our interpretation is unaltered.

(22) J. D. Roberts and R. J. Mazur, *J. Amer. Chem. Soc.*, **73**, 3542 (1951).

(23) R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. C. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).



equilibrating bicyclobutonium ions



equilibrating "bisected" cyclopropylcarbinyl cations

methylcyclopropylcarbinyl (7) < cyclopropylcarbinyl (6). All of the cyclopropylcarbinyl cations show delocalization of charge by the cyclopropyl ring, but only with the primary system do we observe the truly unique behavior which indicates the limiting nonclassical nature of the ion. Present work reinforces our contention that the ^{13}C chemical shifts are an excellent, direct experimental way of determining the "nonclassical" character of carbonium ions.

Acknowledgment. Support of this work by a grant of the National Science Foundation is gratefully acknowledged.

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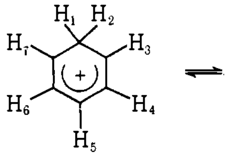
Received October 2, 1969

Stable Carbonium Ions. IC. The Benzenonium Ion ($C_6H_7^+$) and Its Degenerate Rearrangement[1]

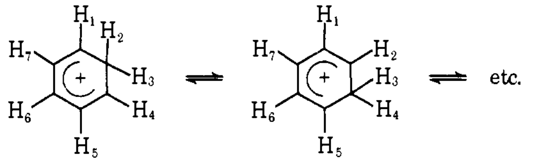
Sir:

Mass spectroscopic studies[2] have shown the formation of $C_6H_7^+$ as a fragmentation ion produced upon electronic bombardment of benzyl alcohol. Substantial research has been reported on proton-addition complexes of aromatic hydrocarbons.[3-12] Olah and Kuhn[6,9] achieved the synthesis and isolation of stable alkylbenzenonium fluoroborate and fluoroantimonate salts. Although Perkampus and Baumgarten[13] reported solid-state infrared and ultraviolet spectra for the ternary system benzene–HCl–$GaCl_3$, a well-characterized description of $C_6H_7^+$ in solution has not been presented until now.[14]

We wish to report the observation of the simple benzenonium ion ($C_6H_7^+$) as a stable long-lived species. When a saturated solution of benzene in sulfuryl chloride fluoride at −50° is added dropwise with vigorous stirring to a 1:2 (v/v) solution of 1:1 (mol/mol) hydrogen fluoride–antimony pentafluoride in SO_2ClF at −78°, a suspension is formed. The clear supernatant solution has a pmr spectrum (Figure 1) consisting of a single sharp peak at δ 8.09 (apart from the acid and the H_3O^+ peaks), which we assign to the degenerate $C_6H_7^+$ ion **1a–c**, undergoing rapid hydrogen migration.



1a



1b **1c**

When the mixed solvent system SO_2ClF–SO_2F_2 was employed,[15] the pmr spectrum could be observed at as low a temperature as −134°. At this temperature the separate absorptions for the four different types of protons of the "frozen-out" benzenonium ion are apparent (*cf.* **1a**): the methylene protons (H_1, H_2) giving a broad signal at δ 5.84, H_4 and H_6 at 8.40, H_5 at 9.20, and H_3 and H_7 at 9.42 ppm (Figure 2). Warming the solution to −70° regenerates the singlet absorption at δ 8.09 ppm.

The temperature dependence of the spectrum was used to calculate the rate constants and activation parameters of the hydrogen migration. The line shapes for various rate constants were calculated and recorded by means of a multiple-site exchange program.[16] The axial (C_{2v}) symmetry of the ion allowed us to treat this case as a four-site problem. Fitting the data to the Arrhenius equation gave an activation

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[1] Part XCVIII: G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *J. Amer. Chem. Soc.*, **92**, 2544 (1970).

[2] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectroscopy of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 119.

[3] V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).

[4] C. Reid, *J. Amer. Chem. Soc.*, **76**, 3264 (1954).

[5] D. A. McCauley and A. P. Lien, *ibid.*, **73**, 2013 (1951).

[6] G. A. Olah and S. J. Kuhn, *Nature*, **178**, 693 (1956); *J. Amer. Chem. Soc.*, **80**, 6535, 6541 (1958).

[7] W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Taber, *Tetrahedron*, **4**, 178 (1958).

[8] E. L. Mackor, A. Hofstra, and J. H. van der Walls, *Trans. Faraday Soc.*, **54**, 186 (1958).

[9] G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 1103 (1965).

[10] C. MacLean and E. L. Mackor, *Discuss. Faraday Soc.*, **34**, 165 (1962).

[11] T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964).

[12] E. M. Arnett and J. W. Larsen, *J. Amer. Chem. Soc.*, **90**, 792 (1968).

[13] H. H. Perkampus and E. Baumgarten, *Angew. Chem. Int. Ed. Engl.*, **3**, 776 (1964).

[14] The species thought to be $C_6H_7^+$ in SO_2 solution of benzene–HF–SbF_6[9] was obviously the sulfinated product (*vide infra*).

[15] The solution (0.5 ml) is added to SO_2F_2 (*ca.* 0.2 ml) in an nmr tube at −78°.

[16] The Fortran IV program was written by C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965), and adapted for use on a Univac 1108 computer by Mr. W. Heyd of this department.