Stable Carbocations. CXIV.[1] The Structure of Cyclopropylcarbinyl and Cyclobutyl Cations[2]

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Abstract: Stable, long-lived cyclopropylcarbinyl and cyclobutyl cations were studied in SbF_5–SO_2ClF solution at low temperature by ^1H and ^{13}C nmr spectroscopy and structural assignments were made based on the data obtained. The cyclopropylcarbinyl cation, c-$C_3H_5{}^+CH_2$, and, for comparison, the secondary and tertiary cyclopropylcarbinyl cations, c-$C_3H_5{}^+CHCH_3$ and c-$C_3H_5C^+(CH_3)_2$, respectively, were examined under comparable conditions. All of the cyclopropylcarbinyl cations show charge delocalization by the cyclopropyl ring, but only with the primary system is the unique behavior observed which puts it in a class distinct from the secondary and tertiary ions. Using model systems for comparison, we interpret the results as indicative of the nonclassical carbonium ion[1b] nature of the cyclopropylcarbinyl cation involving an equilibrating set of $C_{2,3}$- and $C_{2,4}$-cyclopropylcarbonium ions **5**, with equilibration occurring through a puckered cyclobutenium ion (cyclobutyl cation intermediate or transition state). A similar conclusion is reached for the structure of the 1-methylcyclopropylcarbinyl cation, the equilibration for this species occurring *via* a fully formed cyclobutyl intermediate of sufficient lifetime to undergo conformational ring equilibration. The first classical static cyclobutyl cation, the 1-phenylcyclobutyl cation, was also observed and studied by nmr spectroscopy. These data provide direct experimental justification for distinction between trivalent carbenium ("classical") and pentacoordinated carbonium ("nonclassical") ions.

Bartlett has stated: "Among nonclassical ions the ratio of conceptual difficulty to molecular weight reaches a maximum with the cyclopropylcarbinyl–cyclobutyl system." [3]

Much experimental and theoretical work has been devoted to the nature of the cationic intermediate involved in cyclopropylcarbinyl, cyclobutyl, and homoallylic interconversions.[4] Indeed the cyclopropylcarbinyl system has occupied a position of special importance in the "classical–nonclassical" debate.[5] Historically, the term "nonclassical" was first used by Roberts and Mazur[6] to describe the nature of the cationic intermediate (tricyclobutonium ion) involved in reaction of cyclopropylcarbinyl derivatives. In subsequent work, Roberts and coworkers[7] revised their view and favored a rapidly equilibrating set of nonclassical bicyclobutonium ions instead of a single nonclassical species. For substituted cyclopropylcarbinyl cations, the "bisected" structure has received backing.[8,9] More recently Wiberg suggested[10] a puckered cyclobutyl-type, C_s symmetric intermediate which is also supported by work of Baldwin and Foglesong.[4c,11] Various structures for the unsubstituted cyclopropylcarbinyl cation (cyclobutyl cation) have been the basis of theoretical calculations,[12] but general agreement on structure has not been reached.

In contrast to the nonclassical structure of the cyclopropylcarbinyl cation is the view held by some investigators, most succinctly described by Brown in 1962 with reference to a rapidly equilibrating set of nonclassical bicyclobutonium ions ". . . It does not appear to be possible at the present time to distinguish these experimentally from the corresponding set of equilibrating classical ions." [13]

The primary goals of our comprehensive investigation of carbocations[1b] which includes trivalent (classical) carbenium ions as well as tetra- and/or pentacoordinated (nonclassical) carbonium ions were: (1) direct observations of long-lived species and (2) structural determinations by spectroscopic and chemical studies. It has *not* been our aim to determine whether the three-center bound carbonium ions (if formed) under stable conditions are the same ions involved in solvolytic reactions. Rather, our efforts have been directed toward establishing the very existence of long-lived, tetra- and/or pentacoordinated ions, which implies a probe for distinguishing them from the "classical" trivalent carbenium ions. Such distinctions can now be made on the basis of direct experimental spectroscopic data.[14] Our attention in this paper is focused on cations generated from cyclopropylcarbinyl and cyclobutyl derivatives in strongly acidic, weakly nucleophilic media.

In previous work[14] from this laboratory, proton and carbon-13 magnetic resonance parameters of a substantial number of well-defined carbenium ions as well

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(1) (a) Part CXIII: G. A. Olah, P. R. Clifford, and C. L. Jeuell, *J. Amer. Chem. Soc.*, **92**, 5531 (1970). (b) For a detailed discussion of the general concept of carbocations, including differentiation of trivalent (classical) carbenium ions from penta- (tetra-) coordinated (nonclassical) carbonium ions, see G. A. Olah, *ibid.*, in press. This paper also suggests a systematic naming of the ions in accordance with IUPAC rules, which is used in this paper.

(2) For a preliminary communication, see G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

(3) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965, p 272.

(4) For reviews and leading references see (a) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe III, in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. III, Wiley-Interscience, New York, N. Y., in press; (b) C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4274 (1970); (c) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303, 4311 (1968); (d) M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967).

(5) See P. D. Bartlett in ref 3.

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

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

(8) P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

(9) M. Vogel and J. D. Roberts. *ibid.*, **88**, 2262 (1966).

(10) (a) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); (b) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **90**, 4195 (1968); **92**, 571 (1970).

(11) Z. Majerski and P. v. R. Schleyer, *ibid.*, **93**, 665 (1971).

(12) H. Kollmar and H. O. Smith, *Tetrahedron Lett.*, **36**, 3133 (1970).

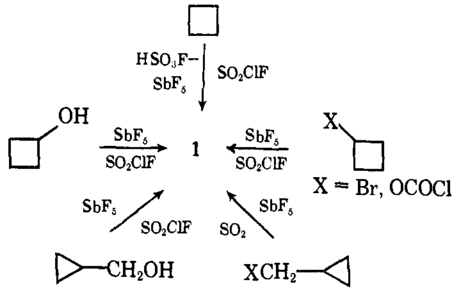
(13) H. C. Brown, *Chem. Soc., Spec. Publ.*, No. 16, 154 (1962).

(14) (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969); (b) G. A. Olah, R. D. Porter, and D. P. Kelly, *ibid.*, **93**, 464 (1971).

as the first carbonium ions have been examined. Relationships of the carbon-13 chemical shifts and ^{13}C–H coupling constants to geometry and electronic density have been demonstrated, and the usefulness of these relationships to characterize organic cations now has a solid basis. This approach has proved successful for distinguishing between: (a) static and equilibrating (degenerate) ions and (b) open-chain (classical, trivalent), and (c) bridged (nonclassical, tetra- and/or pentacoordinated) and (d) bridged (classical) cationic structures. The degree of positive charge delocalization in marginal systems exhibiting characteristics of carbenium and carbonium ions (partial or incomplete σ delocalization)[14a] may also be estimated from cmr studies. Accordingly we set out in the present investigation to answer the following questions. (1) Are long-lived cyclopropylcarbinyl and cyclobutyl cations formed under stable ion conditions? (2) If so, can we distinguish, based on the model ions available, between the possible range of carbenium and carbonium ion structures one must consider in studying these systems?

Results

A. The Cyclopropylcarbinyl Cation 1. 1. Preparation. Our first reported efforts[15] to generate a stable cyclobutyl cation were in 1968, when we observed with Lukas a solution of cyclobutane in $HSO_3F–SbF_5–SO_2ClF$ at −100° to give a pmr spectrum assignable to the cyclopropylcarbinyl cation **1**. Resolution of the low-field absorptions was poor, and above −100° rearrangements occurred. At that time it was recognized that sufficient data were not obtained to enable the distinction to be made among the possible "classical" and "nonclassical" carbocation structures. Subsequently, Lin[16] observed the same ion, prepared by extraction of either cyclopropylcarbinyl or cyclobutyl bromide from carbon disulfide into $SbF_5–SO_2$ solution. Ionizing the chloroformates in $SbF_5–SO_2ClF$ gave similar results, but in all cases the presence of impurities did not allow clear structural characterization. The cyclopropylcarbinyl ion **1** can be generated in good purity from cyclopropylcarbinol or from cyclobutanol in $SbF_5–SO_2ClF$ solution. Attempts to prepare the ion cleanly from allylcarbinyl precursors have failed, apparently due to complexation of the ethylenic bond by SbF_5, thereby making ionizations difficult and allowing side reactions.[16] Quenching −78° solutions of the ions by addition to a rapidly stirred 10% K_2CO_3-buffered ice water–ether mixture gives a mixture of products of which about 60% (glpc) is comprised of about a 4:1 ratio of cyclobutanol to cyclopropylcarbinol. The remaining material was not identified other than to exclude allylcarbinol and 2-methylallyl alcohol.



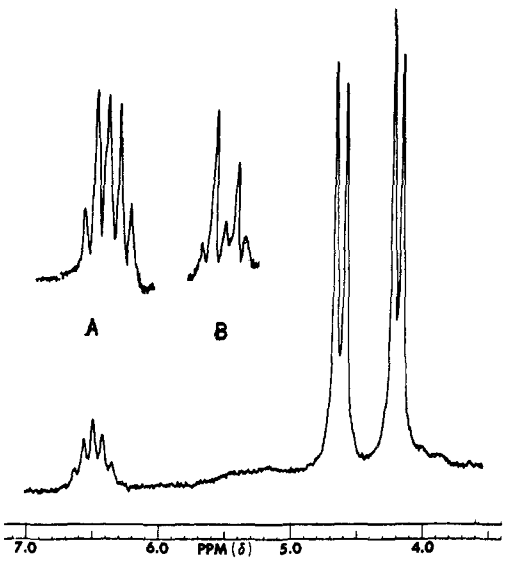


Figure 1. 100-MHz pmr spectrum of the cyclopropylcarbinyl cation in $SbF_5–SO_2ClF$ solution at −80°: (A) 60-MHz spectrum of H_2 region; (B) 60-MHz spectrum of H_2 region from the α,α-dideuteriocyclopropylcarbinyl precursor.

2. Proton Magnetic Resonance Studies. The pmr spectrum of the cyclopropylcarbinyl cation **1** (Figure 1) shows two three-proton methylene doublets, one at δ 4.21 (J = 6.5 Hz) and the other at 4.64 (J = 8.0 Hz), and a one-proton methine multiplet at 6.50. Decoupling experiments reveal that the methine multiplet is made up of two overlapping quartets with J = 8.0 and 6.5 Hz. Comparison is made to the pmr spectrum of the ion obtained upon ionization of α,α-dideuteriocyclopropylcarbinol, the intensity of the methylene doublets being decreased by one-third. The methine multiplet consists of overlapping triplets.[17] The absorption at 60 MHz of the ion **1** at δ 6.50 is shown in insert A of Figure 1. Shown for comparison (insert B) is the methine region absorption observed for the ionized α,α-dideuterio compound.

3. Carbon-13 Magnetic Resonance Studies. The complete 25.1-MHz carbon-13 nmr (cmr) spectrum of the cyclopropylcarbinyl cation was obtained at −70° by the indor technique[14] using time averaging in some cases.[14b] The spectrum shows equivalent methylene absorptions at $\delta_{^{13}CS_2}$ +138 ± 1 ppm with $J_{^{13}CH}$ = 180 ± 5 Hz. The methine carbon appears at +85 ppm, but the $J_{^{13}CH}$ coupling constant was not obtainable by the experimental technique used. From the pmr and cmr spectra we conclude that there are two sets of equivalent protons, both of which are coupled to equivalent carbon atoms.

4. Comparison of Experimental Nmr Data of Ion 1 with Those of Model Ions. To infer structural characteristics to ion **1**, alternative assumed structures **2–8** are presented for consideration. These are reasonable structures which may occur from ionization of cyclobutyl, cyclopropylcarbinyl, and allylcarbinyl precursors (although as already mentioned in the case of the latter we have not met with success in obtaining the ion cleanly by this route). The classical (trivalent) structures are: (a) the classical cyclopropylcarbenium ion **2** which

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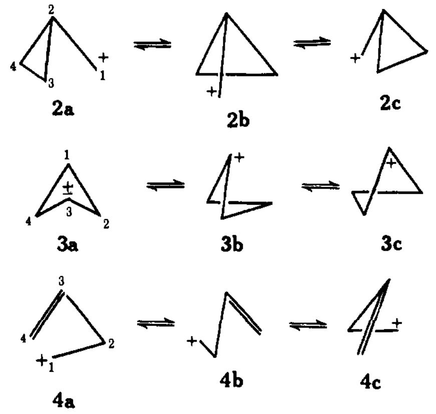
[15] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, 90, 933 (1968).

[16] C. H. Lin, Ph.D. Dissertation, Case Western Reserve University, Cleveland, Ohio, 1969.

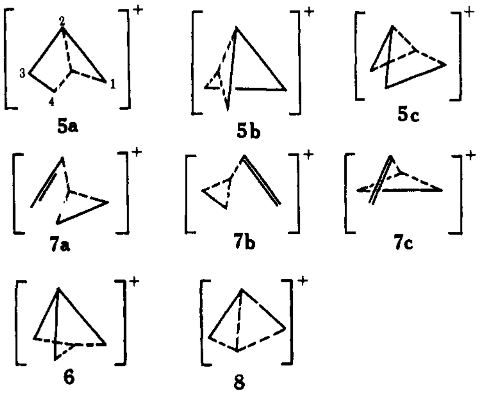
[17] This experiment was carried out by Dr. J. M. Bollinger.

must, based on our nmr data which indicate either high symmetry or rapid equilibrium, exist as the rapidly equilibrating set of ions **2a–c**, (b) the secondary cyclobutyl cation **3**, which also must exist (to satisfy nmr data) as a rapidly equilibrating set of ions **3a–c**, and (c) the primary allylcarbenium ion **4** (**4a–c**).[18]

Carbenium ions



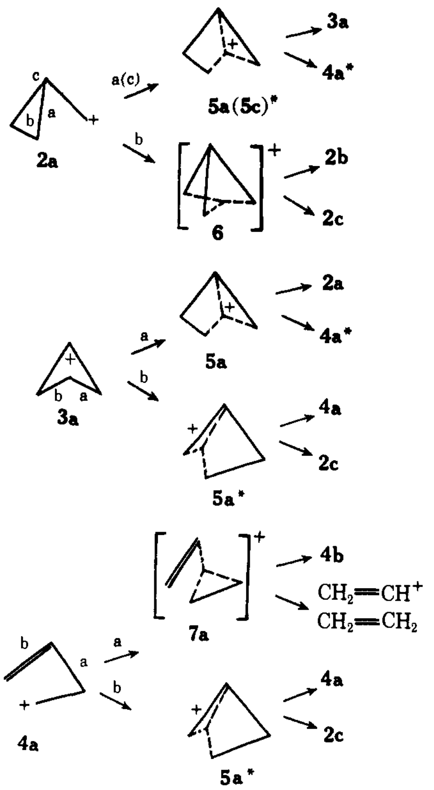
Carbonium ions



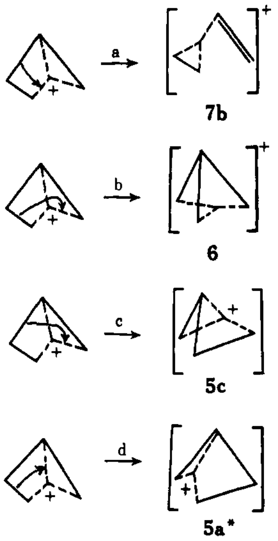
The assumed model ions **2–4** are trivalent carbocations (carbenium ions), the cmr characteristics of which can be accurately estimated from studies on a number of related stable, long-lived cations of known structure.

More difficult is to estimate assumed "nonclassical" carbonium ions. These ions may be pictured as arising from overlap of the carbenium carbon empty p orbital in ions **2** or **3** with a C–C σ bond and in ions **4** with either a C–C σ or π bond (Scheme I). All structures derived in this way result in ions in which the two electrons of the original bond are shared among three carbon atoms.[19] Similar carbonium ions must exist along the reaction path in assumed interconversions of carbenium ions **2–4**, as well as in conversions within the framework of ions **2**, **3**, and **4**.

Scheme I



Scheme II



In Scheme I a simplified representation of the conversion of ions **2–4** to the corresponding carbonium ion structures *via* overlap of the empty carbenium carbon atom p orbital with the bond is presented (C–H bond delocalization to form bicyclobutonium ions [protonated bicyclobutanes], although possible, is not presented here).[20] The resulting three-center bound carbonium ions may open up to the related trivalent carbenium ions which then, *via* delocalization of another bond, could give another related carbenium ion. Rearrangement directly in a more concerted step to another related carbonium ion (*cf.* Scheme II) which would avoid the necessity of going through formally primary carbenium ions is also possible. It should be recognized, however, as also supported by recent theoretical work of Pople and Schleyer,[21] that "primary

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[18] Note that ions **4a–c**, **5**, and **7** are optically active isomeric structures and other structures than those drawn are possible. We are not introducing these into our schemes, except where unavoidable, because it adds additional complexity to an already complex problem, and does not affect the conclusion.

[19] For a comprehensive explanation of the role of the three-centered bond in carbocation chemistry see ref 1b.

[20] Interconversion of carbonium ions may take place *via* intramolecular polytopal-type rearrangements (ref 1b). Conversions of these $C_4H_7^+$ ions to the protonium ions are not included in the discussion. From nmr studies it is clear that they are not representative of the ions under consideration.

[21] (a) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970); (b) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **93**, 1813 (1971). We thank Professor Schleyer for the preliminary communication of these data.

Table I. Nmr Parameters of Cyclopropylcarbinyl Cations[a]

	$\delta(^1H)(J_{H-H})^b$				$\delta(^{13}C)(J_{^{13}CH})^c$			
	Alkyl		Cyclopropyl					
Ion	CH_3	$+CH$	CH_2	CH	CH_3	CH_2	CH_2	C^+
1			4.21 (6.5) 4.64 (8.0)	6.50 (6.5, 8.0)		+138 (180)	+ 85	
9	3.34 (6.2)	9.6 (6.2)	4.32 4.45	4.58	+160	+136	+126	−59.1
10	2.70, 3.18 (1.25)		3.57 3.68	3.83	+154 (125) +163 (125)	+140	+134	−86.8

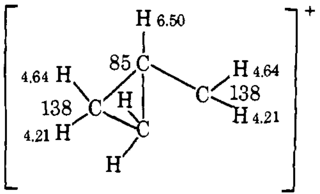
[a] Determined at 100 MHz at −70° in SbF_5–SO_2ClF solution. [b] Parts per million from external TMS, *J* in hertz. [c] Parts per million from $^{13}CS_2$ *via* indor.

ions" in all probability always represent energy minima involving at least some partial bond delocalization (*via* three-center bond formation). It is thus becoming clear that no limiting differentiation of two separate routes seems justified without further clarification of the bonding concepts. Ions **5–7** can be derived from the tri-center bonded carbonium ion, as well as from the related carbenium ions. Such a process is shown for ion **5a** in Scheme II where the cleavage of the three-center bond is followed by delocalization of the developing carbenium ion center by another C–C single bond.[20] Such processes can eventually equilibrate all methylene carbons. **5a** gives rise through routes c and d to **5c** and **5a*** (the optical isomer of **5a**). This places the three methylene carbons in all three environments (discussed later) over the entire equilibration scheme, although only three of the six isomers of ions **5** are observed in the equilibrium. Such a process could be pictured as well for any member of the series **5a–c**, **6**, and **7a–c**, although the **7** isomers must be formed *via* a more circuitous route. Ion **8** is mentioned because of its "popularity,"[22] the formation of which, along even hypothetical pathways, is conceptually difficult.

Our efforts, as outlined, are directed toward inferring the structure to ion **1** by correlating its observed spectral parameters with those estimated from suitable models for the assumed ions **2–8**.

(a) **Comparison of the Cyclopropylcarbinyl Cation with Classical Cyclopropylcarbenium Ion Models.** In order to assess the utility of nmr parameters for determining the nature of the parent (unsubstituted) cyclopropylcarbinyl cation **1**, we compared proton and carbon-13 shifts of cyclopropyl- (**1**), methylcyclopropyl- (**9**), and dimethylcyclopropyl- (**10**) carbenium ions.[23]

For ready comparison, proton and carbon-13 chemical shifts[23b] of the ions are shown on the structures (^{13}C chemical shifts are displayed in boldface type). Nmr parameters are summarized in Table I. The pmr spectrum of ion **9** is shown in Figure 2. The dimethylcyclopropylcarbenium ion **10** has been reported in our previous studies[14a,24] but additional and improved data have now been obtained. The ^1H spectrum of the ion **10** displayed in Figure 3 shows fine structure of the methyl signals due to coupling through the carbocationic center.



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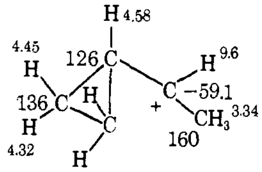

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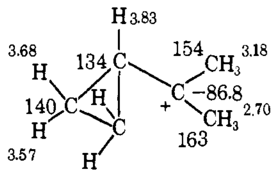

10

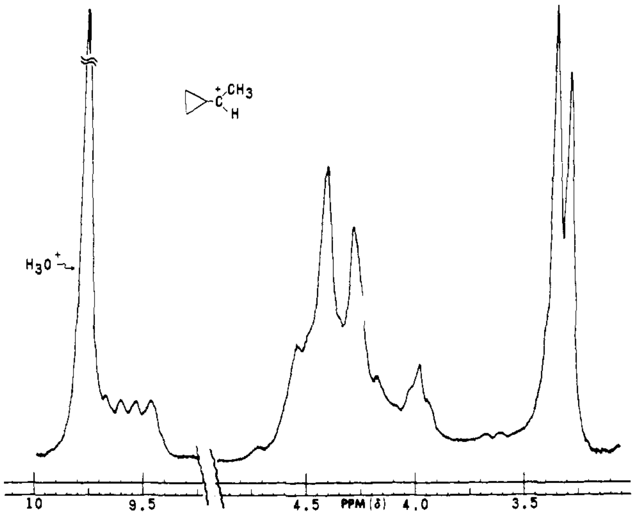

Figure 2. 100-MHz pmr spectrum of the methylcyclopropylcarbinyl cation **9** in SbF_5–SO_2ClF solution at −70°.

We obtained the complete cmr spectrum of each of the ions **1**, **9**, and **10** because it was clear from the prior studies that factors responsible for ion stabilization could not be described on the basis of proton spectra alone.

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(22) Ion **8**, the C_s symmetric species, has a poorly defined bonding scheme. CNDO calculations by Wiberg[10] predicted the C_s symmetry to be favorable. More recently E. I. Snyder (*ibid.*, **92**, 7529 (1970)), in treating β-phenylethyl systems, demonstrated serious inconsistencies to arise when applying CNDO calculations on small ring systems. Baldwin and Foglesong[4c] supported the C_s symmetric species *via* EHT calculations while acknowledging that their accuracy has been subject to much doubt (*cf.* M. J. S. Dewar, *Chem. Soc., Spec. Publ.*, No. 21 (1967)).

(23) (a) As a working hypothesis for this comparison, all of the alkylcyclopropylcarbinyl cations (**1**, **9**, and **10**) are shown (and referred to) here as classical (carbenium) ions. However, see following discussion for consideration of their structure. (b) ^1H chemical shifts are in parts per million relative to TMS. Carbon-13 chemical shifts are in parts per million relative to $^{13}CS_2$. Negative cmr shifts are to low field of $^{13}CS_2$.

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

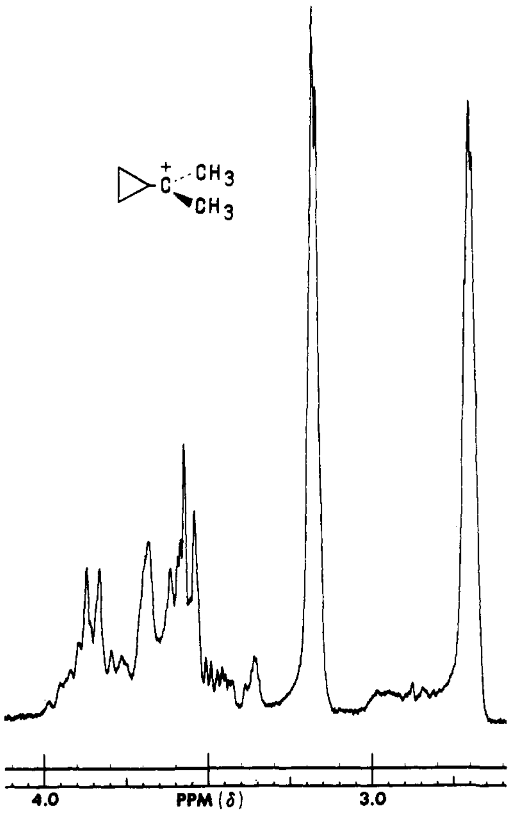


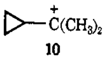
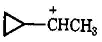
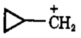
Figure 3. 100-MHz pmr spectrum of the dimethylcyclopropylcarbinyl cation **10** in SbF_5–SO_2 solution at −60°.

Comparison of the cmr shifts of the electron deficient (sp^2) carbenium atom in ions **9** and **10** ($\delta(^{13}C)$ −59 and −87 ppm) with those of isopropyl (−125) and tertiary butyl (−135) cations, respectively,[14] indicates significant delocalization of positive charge by the cyclopropyl group.

It is known that replacement of a methyl group by a hydrogen atom produces about a 10-ppm shielding effect on the cmr shift of sp^2- as well as sp^3-hybridized carbons.[25] In the case of ion **9**, such a replacement on the carbenium carbon of a proton by a methyl substituent causes a more marked shielding effect (28 ppm), apparently due to increased σ delocalization in the secondary ion. The problem then regarding the nature of ion **1** can be further specified as one of determining whether the alteration of molecular structure concomitant with charge delocalization is such that ion **1** is in a class distinct from that of ions **9** and **10**. That is, are we dealing with a change in degree (*i.e.*, to ions **2**) or a change in kind in going from ion **10** to **9** to **1**?

A conclusion can be reached based on calculations of the carbon-13 chemical shift of the methylene carbons of ion **1** using appropriate models. To compute an average cmr shift for an equilibrating set of (degenerate) classical cyclopropylcarbinyl ions **2**, values for the cyclopropyl methylene and methine carbons and the primary sp^2-hybridized carbenium atom are estimated. In Table II are listed the pertinent experimentally observed carbon chemical shifts for ions **9** and **10**. Using these values and carrying out a linear extrapolation[26] for the assumed static classical cyclopropylcarbinyl cation **2**, the values (in parentheses) in the last row of Table II were derived.

Table II. ^{13}C Nmr Shifts[a] of the Dimethylcyclopropylcarbenium (**10**) and Methylcyclopropylcarbenium (**9**) Ions and Estimated Values[b] of the Classical, Static Cyclopropylcarbenium Ion **2**

Ion	$\delta_{^{13}C^+}$	$\delta_{^{13}CH_2}$	$\delta_{^{13}CH}$
 **10**	−86.8	+140.4	+134
 **9**	−59.1	+136.3	+126
 **2**	(−31) static	(+132)	(+118)

[a] Parts per million relative to $^{13}CS_2$. [b] See ref 26.

The calculated (average) cmr shift for the methylene carbons of a classical, degenerate cyclopropylcarbenium ion is $[2(132) + 1(-31)]/3 = +78$ ppm, in marked contrast to the experimentally observed value of δ +138 ppm.

An alternate approach is the following: Using the estimated shift (−31 ppm) for the carbenium carbon of the assumed static, classical cyclopropylcarbinyl cation and the experimental value (+138 ppm) for the chemical shift of the methylene carbons in ion **1**, the ^{13}C shift of the ring methylene carbons is computed. Accordingly $[2(X) + 1(-31)]/3 = +138$; $X = +222$ ppm. That is, for a classical, static ion the ^{13}C shift of the cyclopropylmethylene carbons would have to be +222 ppm in order to give the observed shift of +138 ppm (for a classical, degenerate ion). This estimated value is unrealistic, not only when compared with related values in **9** and **10**, but also when compared with cyclopropane itself (+196.3 ppm).[27] Linear extrapolation of the ^{13}C chemical shift of substituted carbon in the cyclopropane ring C_2 to structure **2** from **9** and **10** (see Table II) would give a predicted value for C_2 of $\delta_{^{13}C}$ +118 to compare to our observed value of $\delta_{^{13}C}$ +85. Again, ion **2** is shown not to be compatible with ion **1** and is different from ions **9** and **10** in kind rather than in degree.

(b) Comparison of Ion 1 to the Cyclobutenium Ion (Cyclobutyl Cation) 3. Ion **3** is a secondary carbenium ion and as a stable static species is unacceptable, as the pmr spectrum should result (*e.g.*, for ion **3a**) in a more complex H_2–H_3–H_4 pattern than that experimentally observed for ion **1**. If ion **3** is observed *via* pmr as a time-averaged set of rapidly equilibrating ions **3a** $\rightleftarrows$ **3b** $\rightleftarrows$ **3c**, it can then be seen that C_1 retains its secondary

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(25) (a) B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 5319 (1967); (b) D. M. Grant and E. G. Paul, *ibid.*, **86**, 2984 (1964); (c) L. M. Jackman and D. P. Kelly, *J. Chem. Soc. B*, 102 (1970).

(26) We have completed one study of cmr parameters of a tertiary–secondary–primary ion series differing only in methyl substitution at the carbenium carbon. This study showed a linear extrapolation to be not generally completely valid, although the differences as observed do not negate our result here. The carbenium ion carbon-13 chemical shifts were obtained for the tertiary dimethyl-*p*-methoxyphenylcarbenium ion (δ −25.2) (G. A. Olah, C. L. Jeuell, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3961 (1969)), the secondary monomethyl-*p*-methoxyphenylcarbenium ion (δ −5) (ref 14b), and the parent primary *p*-methoxybenzyl cation (δ +25) (G. A. Olah, R. D. Porter, and C. L. Jeuell, *J. Amer. Chem. Soc.*, in press). Carrying out a parallel extrapolation for **2** where $\Delta\delta$ (tertiary–secondary) gives an estimated cmr difference two-thirds that for $\Delta\delta$ (secondary–primary) as in the para anisyl system will result in an estimate for the methylene carbon-13 chemical shift for the degenerate set of ions **2a–c** of +82 ppm which is still low.

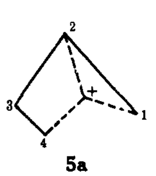
(27) (a) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964); (b) G. E. Maciel and G. B. Savitsky, *J. Chem. Phys.*, **69**, 3925 (1965).

carbenium carbon character. Both pmr and cmr should, therefore, show chemical shifts at the position C_1 (H_1) which are characteristic of secondary alkylcarbenium ions. A suitable model for such a comparison is the dimethylcarbenium ion where at the carbenium site the cmr shift is -125 ppm[14a] and the pmr chemical shift is 13.5.[28] On this basis, model ions **3** do not fit the nmr spectroscopic data obtained for **1**.

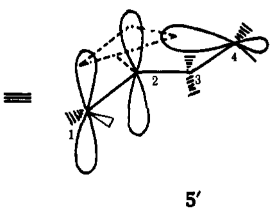
(c) Comparison of 1 to Allylcarbinyl Cations 4. As in the cases of assumed ions **2** and **3**, the simplicity of the pmr spectrum itself dictates that if ion **4** is indeed the observed species, it must be an equilibrating set of degenerate ions **4a–c**. Using **4a** as the basis, C_3 retains its identity and its cmr shift ($+85$ ppm) is shielded relative to an expectedly deshielded ethylenic carbon. This consideration is not by itself compelling in eliminating **4** as a structural possibility. Therefore, estimates for the time-averaged cmr shifts C_1 (carbenium carbon), C_2 (methylene), and C_4 (ethylenic) for ion **4a**, which must exchange identities during rapid equilibration, are calculated. For C_1 the model primary carbenium carbon already developed for cyclopropylcarbenium ion **2a** is used ($\delta_{^{13}\mathrm{C}}$ -31 ppm).[29] C_4 is ethylenic in character and the cmr shift for a terminal vinylidene carbon should suffice (δ $+88$ ppm),[30] while a value for a carbon adjacent to a carbenium carbon is available from the isopropyl cation[14a] (δ $+133$), and is used for the estimate of C_2. Computing the time-averaged methylene cmr shifts from such an equilibrating set of assumed ions, **4** shows $\delta_{^{13}\mathrm{C}} = [(+88) + (-31) + (133)]/3 = +63$ ppm. This value is to be compared with our experimentally obtained value of $+138$ ppm. The comparison shows ions **4a–c** to be an unacceptable assignment for the observed spectra of **1**.

(d) The $C_{2,3}$- and $C_{2,4}$-Cyclopropylcarbonium Ions 5. The cyclopropylcarbonium ions **5** can be formed from cyclopropylcarbenium ions by C_2–C_3 or C_2–C_4 bond delocalization *via* two-electron three-center bond formation with the empty p orbital of carbenium carbon at C_1. The ^{13}C chemical shift of the methylene carbons of the "nonclassical" cyclopropylcarbonium ion **5** can be calculated with the aid of the known nonclassical norbornonium ion **11** which has been completely characterized[31,32] and is shown for comparison with ion **5a**.

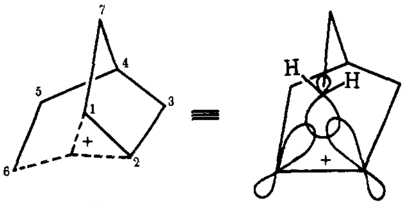
The approach is analogous to that taken for the previous estimates for **2a–c**. The static nonclassical structure **5a** is assumed for the ion, cmr chemical shift values are assigned to the methylene carbons based on model estimates, and an average ^{13}C shift resulting from time averaging of the carbons C_1, C_3, and C_4 during fast equilibrating of the nonclassical **5a–c** is computed.



5a



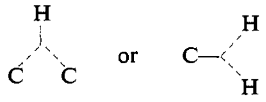
5′



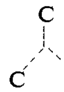
11

Estimates of cmr values of the methylene carbons, C_1, C_3, and C_4, of **5** are as follows: C_1 (in **5a**) $\delta_{^{13}\mathrm{C}}$ $+80$ ppm, since this carbon bears formal similarity to C_1 ($\equiv C_2$), $\delta_{^{13}\mathrm{C}}$ $+70$ ppm, in the norbornonium ion **11**,[32,33] used as the model. Ten parts per million are added to the shift ($+70$) in the norbornonium ion since a methylene bridge, *i.e.*, C_7 in **11**, is formally replaced by a hydrogen atom is **5a**.[25,33] C_3 (in **5a**) has analogies in C_3, C_5, and C_7 in ion **11**, the time-averaged cmr shift of these three carbons (δ $+162$) being used as the model.[34] C_4 (in **5a**) is comparable to the C_6 carbon ($+173$) of ion **11** and this value is used here. Assuming the **5a–c** equilibration, calculation of an average shift gives $[(80) + (162) + (173)]/3 = 138$ ppm, in exact agreement with the observed shift ($+138$), although we realize this degree of accuracy to be fortuitous.

The Question of Bicyclobutonium Ions. When considering, from a purely hypothetical point of view, the ways in which a proton could be attached to bicyclobutane to form bicyclobutonium ions, there are two C–C bonds into which insertion would be possible (to form 1,3- or 1,2-*C*-bicyclobutonium ions) and similarly two C–H bonds (which would lead to 1- and 2-*H*-bicyclobutonium ions, respectively). The latter, in all probability, could represent only relatively high energy transition states. This is analogous to arguments developed in the question of cycloproponium ions. The three-center bonds involved in these bicyclobutonium ions would be



The cyclopropylcarbonium ion, which also can be considered in accordance with general usage as a bicyclobutonium ion, however, has methylene-bridged structures involving



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[28] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. MacIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964).

[29] Realistically, this value is much too shielded; all present evidence would indicate a primary alkylcarbenium carbon to have a cmr shift of δ -100 (tertiary butyl, δ -135; isopropyl, δ -125, see text).

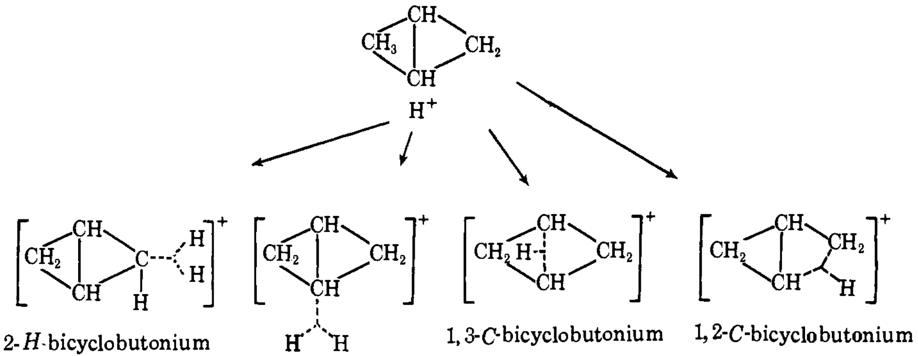
[30] The value of δ $+88$ was the highest in a series of vinylidene cmr shifts. Extensive cmr shifts for alkenes were recorded by G. B. Savitsky and K. Nakimura, *J. Phys. Chem.*, **68**, 1956 (1964). The vinylidene cmr shifts reported were from δ $+78.6$ to $+88.0$ and selection of a lower value would cause the estimate of ion **4** to be further removed from the observed value for **1**.

[31] The conformation **5** is the same as that proposed by Roberts and coworkers[7] (see also M. E. H. Howden and J. D. Roberts, *Tetrahedron, Suppl.*, No. 2, 403 (1963)). The slight modification in **5** (*cf.* formulation of Roberts and coworkers) is that C_4 maintains tetrahedral hybridization.

[32] G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).

[33] In using the norbornyl cation **11** to estimate cmr shifts for the $C_{2,3}$-cyclopropylcarbonium ion **5**, we have neglected that **11** is a symmetrically bridged structure while **5** is unsymmetrically bridged. There are as well obvious differences in strain between **11** and **5**.

[34] As obtained for **11** in ref 32, C_3, C_7, and C_5 were time averaged and C_3 and C_7 were different from C_5 as "frozen out" (they were not obtained individually). As we depict C_3 in ion **5a** here, it has characteristics of all carbons (C_3, C_5, and C_7) in **11**; therefore, it is considered a reasonable choice for an estimate.



2-*H*-bicyclobutonium ion

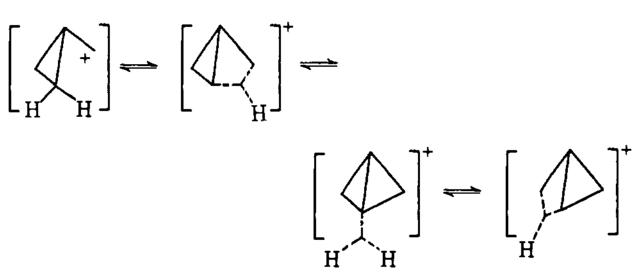
1-*H*-bicyclobutonium ion

1,3-*C*-bicyclobutonium ion

1,2-*C*-bicyclobutonium ion

three-center bonding. They are formed *via* C–C bond delocalization from cyclopropylcarbinyl or cyclobutyl cations, as discussed.

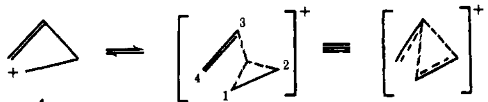
As in the case of the 1-propenium ion–cyclopropoponium ion–ethylenemethonium ion systems,[1b] the cyclopropylcarbenium ion–cyclopropylcarbonium ion system also could be considered to undergo C–C as well as C–H bond delocalization, giving protonated bicyclobutanes. The latter process, however, would equilibrate all protons (and carbons) if the bridgehead bicyclobutane methine group could be involved in 1-*H*- as well as 1,3-*C*-bicyclobutonium ion formations. Experimental facts are to the contrary as shown by our pmr studies here with the deuterium substitution which agrees with similar labeling studies carried out by others under solvolytic conditions.[7,35] Thus, in accordance with experimental evidence, the equilibration is considered to proceed through C–C bond delocalized *C*-cyclopropylcarbonium ions, a situation similar to protonated cyclopropane equilibrations.



In the rapidly equilibrating *C*-cyclopropylcarbonium ion system, the three-center bonding always involves a pentacoordinated and two tetracoordinated carbonium carbon atoms, similar to the norbornonium ion. It is interesting to point out further that if the methine C_2–H bond could overlap with the p orbital on C_1, subsequent 1,2-hydrogen shift would lead to the trivalent methylcyclopropyl cation, which would be expected to open up to the allylic ion. Such an overlap is not possible in the generally preferred "bisected geometry" of cyclopropylcarbenium ions. However, slight steric effects, like a methyl group in case of the α-methylcyclopropyldimethylcarbonium ion, could cause the "in-plane" geometry to become favored over the "bisected" one. Consequently, the 1,2-methyl shift occurs readily followed by ring opening to the tertiary butyl allyl cation (see subsequent discussion).

(e) The Tricyclobutonium Ion, C_2–C_3-Cyclopropylcarbonium Ion 6. This ion can be seen to formally arise from C_3–C_4 bond delocalization with the empty p orbital at the C_1 carbenium ion center in ion **2** (Scheme I). Whereas orbital symmetry would allow formation of ion **6**, the tetrahedrane-like geometry needed for overlap would be too strained and would prevent participation of the C_3–C_4 bond. The cmr shifts of hypothetical ion **6** cannot be estimated because a totally symmetric structure for a carbonium ion with three carbon atoms equally sharing a bonding electron pair as yet has no precedent in stable ion systems. CNDO calculations, unreliable as they may be in small ring systems,[22] have demonstrated an ion of the type **6** in these systems to be destabilized by 150 kcal/mol^{-1}.[10b]

(f) The Symmetrically Bisected Ion, $C_{2,3}$-Allylcarbonium Ion 7. Ion **7** has been pictured as **7′** and can be depicted in terms of C_2–C_3 σ bond delocalization with the empty p orbital of the carbenium carbon in the allylcarbenium ion **4** (Scheme I) or, for example, path a in Scheme II. The two ions, as they are depicted, differ in that **7′** implies a more extended "nonclassicality," wherein in the framework of carbocation chemistry, **7** can be seen as a $C_{2,3}$-allylcarbonium ion with allylic C_3–C_4 positive charge stabilization of the three-centered bond. For clarity, this allylic stabilization, being of a different type, is best not pictured as a dotted line.



4a **7** **7′**

The carbon C_1 and C_2 chemical shifts found in the norbornonium ion **11** are used again as models for C_1 and C_2 of ion **7** along with substituent corrections for "loss" of the alkyl groups which form the backbone of ion **11**. The substituent effect of alkyl groups relative to hydrogen is assumed to be approximately that of the methyl substituent, and to deshield cmr shifts of the substituted carbon by about 10 ppm.[25] This gives an estimated chemical shift for $C_1(C_2)$ of $\delta_{^{13}\mathrm{C}}$ (+70 + 10 = +80 ppm). C_4 is estimated from known data of terminal carbons in allyl cations[36] to be −53 ppm. The total estimated cmr shift for the time-averaged equili-

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[35] (a) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960); (b) E. Renk and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 878 (1961); (c) K. L. Servis and J. D. Roberts, *ibid.*, **86**, 3773 (1964); (d) Z. Majerski and P. v. R. Schleyer, *ibid.*, **93**, 665 (1971).

[36] G. A. Olah, P. R. Clifford, Y. Halpern, and R. G. Johanson, *ibid.*, **93**, 4219 (1971). Only tertiary and secondary C_1 cmr shifts for alkylallyl cations have been determined (for 1,3-dimethylallyl, $\delta_{^{13}\mathrm{C}}$ = −47 ppm; for 1,1,3,3-tetramethylallyl, δ = −41). For our purposes here we assume the estimated shift to be an extrapolated value (to the unsubstituted allyl cation, δ = −53 ppm).

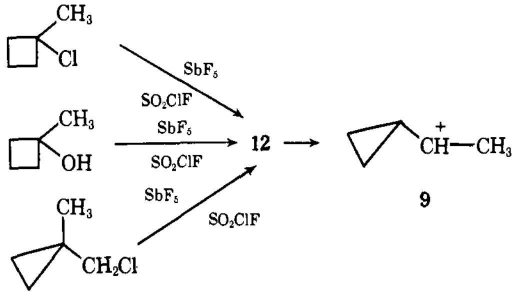
brating set of ions **7** is $[2(+80) + 1(-53)]/3 = +36$ ppm. If, on the other hand, the assumption is made that the C_4 carbon in **7** is ethylenic in character (estimated cmr shift for vinylidene carbons [+88])[30] the time-averaged methylene carbon shift is calculated as $[2\cdot(+80) + (+88)]/3 = +85$, which is still unsatisfactorily low when compared with the experimental value of **1**.

Considering the bonding concept, it is difficult to visualize why the C_2–C_3 σ bond should delocalize the empty p orbital of the C_1 carbenium atom instead of the C_3–C_4 π-electron pair, to give the cyclopropylcarbonium ion **5**. When orbital symmetry and geometric consideration allow both, a π-electron pair should be a much stronger internal nucleophile than a σ pair.

(g) The C_s Symmetric Ion 8. From available data at hand, calculation of ion **8** is not possible. CNDO calculations of Kollmar and Smith[12] present evidence for strong interactions of the C_2–C_3 and C_2–C_4 bonds with the carbenium carbon C_1 in the cyclopropylcarbenium ion **2**. Because **2** is constrained in their model to C_s symmetry, the equal delocalization of the C_2–C_3 and C_2–C_4 bonding is demanded, but of the ions calculated by these authors, the **3** analog was considered more stable by 20 kcal mol^{-1}.

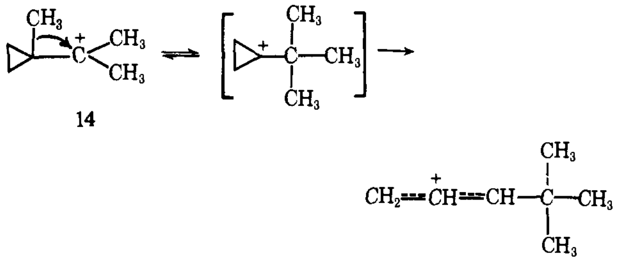
The generation of the other proposed ions **2**–**7** in the studied system is straightforward, ion **5** providing an explanation which fits the experimental data well. At this time, we see no reason to involve a possible four-center bound species, other than as a transition state as in path d (Scheme II, the conversion of **5a** to **5a***).

B. The 1-Methylcyclopropylcarbinyl Cation 12. 1. Preparation and Magnetic Resonance Data. The ion **12** was first reported by Saunders and Rosenfeld[37] who obtained it by low-temperature (−80°) ionization of 1-chloro-1-methylcyclobutane or 1-chloromethyl-1-methylcyclopropane in SbF_5–SO_2ClF solution. The pmr spectrum consists of a quartet at δ 3.89 (6 H, J = 0.9 Hz) and a septuplet at δ 2.87 (3 H, J = 0.9 Hz). Isomerization of ion **12** to the methylcyclopropylcarbenium ion **9** occurs at −25°. Saunders and Rosenfeld also report that ionization of 1-chloro-1-trideuteriomethylcyclobutane produces an ion the nmr spectrum of which shows a singlet at δ 3.93 (CH_2) and no scrambling of protons to the trideuteriomethyl peak as evidenced by essentially no absorption at δ 2.9 being observed.[37]



We have prepared the same 1-methylcyclopropylcarbinyl cation by ionization of 1-methylcyclobutanol at −78° in SbF_5–SO_2ClF solution. Using the indor technique, the cmr spectrum of ion **12** was obtained. The methylene carbons appear at $\delta_{^{13}\mathrm{CS}_2}$ +146 ppm with $J_{^{13}\mathrm{C-H}}$ = 167 Hz, while the methyl-substituted carbon is a singlet at $\delta_{^{13}\mathrm{C}}$ +33 ppm. The methyl carbon resonance is at $\delta_{^{13}\mathrm{C}}$ +170 ppm.

Attempts to prepare the related secondary and tertiary 1-methylcyclopropylcarbinyl cations $1\text{-}CH_3\text{-}c\text{-}C_3H_5{}^+CHCH_3$ (**13**) and $1\text{-}CH_3\text{-}c\text{-}C_3H_5C^+(CH_3)_2$ (**14**), respectively, for spectral comparison instead gave spectra complex in nature, indicating formation of opened allylic ions (details to be reported separately). A possible explanation would be to suggest that the 1-methyl substituent may cause sufficient steric interaction so as to render the bisected conformation of the ions somewhat less favorable than the in-plane conformation. The orbitals which would be involved in a 1,2-methyl shift are thereby in favorable orientation. Subsequent ring opening would produce allylic ions. Allylic cations from cyclopropylcarbinyl derivatives have been reported previously.[37,38] We feel the data can be better explained in terms of the intermediate stability rather than steric effects as explained later.



2. Comparison of Cmr Data to Model Ions. (a) The 1-Methylcyclopropylcarbenium Ions. The experimental value of $\delta_{^{13}\mathrm{C}}$ +146 for the methylene carbons is compared to the value calculated for the classical equilibrating model ions **2** which show little difference upon C_2 methyl substitution. A methyl substituent at C_2 of **2** would have a substituent effect on the cmr shift of C_2 estimated to be a maximum of 10 ppm. This would be expected to result in deshielding for C_2 to about $\delta_{^{13}\mathrm{C}}$ +108 ppm from the value δ +118 estimated for **2a** by extrapolation from ions **9** and **10** (Table II). This again is incompatible with our experimentally observed value of $\delta_{^{13}\mathrm{C}}$ +33 ppm for **12**, and a degenerate classical 1-methylcyclopropylcarbenium ion is ruled out.

(b) The 1-Methylcyclobutenium Ions and 2-Methylallylcarbenium Ions. The methylcyclobutyl tertiary ion is ruled out as well, as the anticipated cmr shift at the tertiary methyl-substituted carbenium carbon is $\delta_{^{13}\mathrm{C}}$ −142 ppm (from data of the related methylcyclopentyl cation).[14a] The 3-methyl analog of allylic open primary ions **4** should have the same estimated time-averaged cmr shift of the methylene carbons as does the ion **4** itself ($\delta_{^{13}\mathrm{C}}$ +63). Comparison with the observed value of δ +146 shows this ion as well to be unsatisfactory as a model.

(c) The Nonclassical Carbonium Ion Models. Estimates for the methylene carbon time-averaged cmr shifts of methyl-substituted analogs of ions **5** and **7** are the same as those made for the unsubstituted ions themselves. Again, ion **5** alone comes closest to the actually observed value and for this reason we assign to ion **12** the structure of the 2-methyl-$C_{2,3}$-cyclopropylcarbonium ion.

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(37) M. Saunders and J. Rosenfeld, *J. Amer. Chem. Soc.*, **92**, 2548 (1970).

(38) T. S. Sorensen and K. Ranganayakulu, *Tetrahedron Lett.*, 659 (1970).

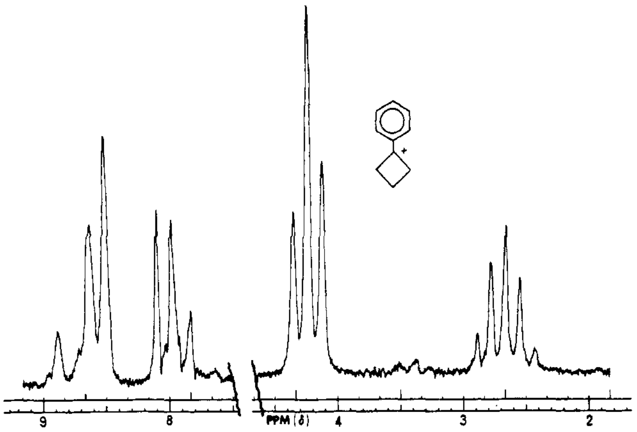
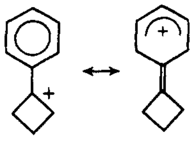


Figure 4. 60-MHz pmr spectrum of the 1-phenylcyclobutyl cation **15** in SbF_5–SO_2 solution at −65°.

If one considers an estimate for C_2 in **12** to be feasible from a substituent effect correction (−10 ppm) for a methyl group on $C_1(C_2)$ on **11**, $\delta_{^{13}C}$(estimated) = +60 ppm. This value is still substantially shielded from the experimentally observed value of $\delta_{^{13}C}$ +33. We suggest ions of the type **3** to play an important role in the chemistry of this ion, with this evidencing itself in the form of unsymmetrically three-centered bound carbons slightly favoring the methylcyclobutenium structure. Equilibration of the 2-methyl-$C_{2,3}$-cyclopropylcarbonium structures must also involve the methylcyclobutenium ion as, barring methyl steric effect (*vide supra*) which would less likely play a role in **12** than in **13** or **14**, a ring flip of the methylcyclobutenium ion will readily effect time averaging of the two sets of three methylene protons.

C. The 1-Phenylcyclobutyl Cation 15. It is clear from the preceding study of ion **12** that a methyl group is not capable of stabilizing a long-lived cyclobutenium ion (cyclobutyl cation) to such an extent that the ion is the most stable of the $C_5H_9^+$ structures in an equilibrium. From previous experience with the 2-norbornyl cation system,[32] together with the work of D. D. Roberts,[39] it seemed that a phenyl group could provide sufficient stabilization for a cyclobutyl cation. Therefore, we ionized 1-phenylcyclobutylcarbinol in SbF_5–SO_2 solution. The pmr spectrum is displayed in Figure 4, showing absorptions at δ 7.82–8.88 (aromatic protons), 4.23 (triplet, J = 3.5 Hz, α-methylene), and 2.66 (pentuplet, J = 3.5 Hz, β-methylene). The cmr shift of the phenyl-substituted carbon is −79 ppm. This value is comparable to the corresponding carbenium carbon in the 1-phenylcyclopentyl cation **16** (−70 ± 2 ppm).[32] These data are consistent with a classical 1-phenylcyclobutyl cation.



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Conclusions

The conclusion that the cyclopropylcarbinyl cation is a three-center bonded carbonium ion is made from the following evidence. (i) The observed ion **1** shows (nmr) two sets of equivalent methylene protons and equivalent methylene carbons showing the ion to be symmetrical (with C_{3v} symmetry) and/or degenerate. (ii) The ^{13}C chemical shift data show ion **1** to be distinctly different from all carbenium ions considered. (iii) Of the considered nonclassical ions for which models exist (**5** and **7**) the data cleanly fit ions **5**, the $C_{2,3}$-cyclopropylcarbonium ion, but not **7**, the $C_{2,3}$-allylcarbonium ion. (iv) Structure **6** is rejected on the grounds of unfavorable highly strained geometry needed to delocalize the C_3–C_4 σ bond and overwhelmingly unfavorable stability in all theoretical calculations, although we have no experimental evidence to rule it out. Ion **8** we cannot deal with experimentally, but feel no need to invoke new bonding concepts which necessitate σ-bond delocalization over four carbon atoms. Positive experimental evidence favors structure **5** for which precedent in long-lived ions is well established.

Carbon-13 magnetic resonance parameters for cyclopropylcarbinyl **1** and 1-methylcyclopropylcarbinyl **12** ions and for 1-phenylcyclobutyl **15** and 1-phenylcyclopentyl **16** ions are summarized in Table III. This tabulation shows the close similarities in the carbon-13 nmr shifts and J values for the methylene carbons of ions **1** and **12** and for the phenyl-substituted cmr shifts of ions **15** and **16**. Based on the foregoing discussion, it is concluded from these data that ions **1** and **12** are "nonclassical" carbonium ions while ions **15** and **16** are "classical" carbenium ions.

Table III. Characteristic ^{13}C Nmr Parameters of Cyclopropylcarbinyl and Phenylcycloalkyl Cations

		$\delta_{^{13}C}$[a]		
Ion	Solvent (T, °C)	C	CH_2[b]	C^+
1	SbF_5–SO_2ClF (−70)	+85	+138 (J_{CH} = 180)	
12	SbF_5–SO_2ClF (−70)	+33	+146 (J_{CH} = 167)	
15	SbF_5–SO_2 (−65)			−78.8
16	HSO_3F (−20)			−70 ± 2[c]

[a] In parts per million from $^{13}CS_2$. [b] J values in hertz. [c] Reference 32.

As is the case in the 2-norbornyl cationic system **11**,[32] we observe both classes of carbocation structures in the cyclobutyl system. Both the unsubstituted norbornyl and cyclobutyl (cyclopropylcarbinyl) ions are carbonium ions. Phenyl substitution in both **11** and the cyclobutyl system **15** allows formation of tertiary carbenium ions. Whereas a methyl group in the 2 position of **11** gives only a partially σ-delocalized ion (due to stabilization from the methyl group), a methyl substituent is not as effective in producing similar stabilization in the cyclobutyl system. Though there is in **12** apparent unsymmetrical character to the three-centered bond favoring the positive charge residing somewhat more at the apex (quaternary carbon) relative to the methine carbon of the unsubstituted species **1**, the ion is a carbonium ion in overall characteristics, *i.e.*, the empty p carbon orbital on the developing carbenium center is delocalized with a suitable C–C bonding σ electron pair in three-center bond formation.

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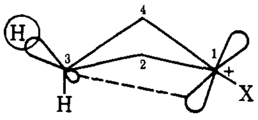
(39) D. D. Roberts, *J. Org. Chem.*, **34**, 285 (1969).

Of the various nonclassical formulations proposed for cyclopropylcarbinyl cations, we favor equilibrating $C_{2,3}$- and $C_{2,4}$-cyclopropylcarbonium ions with the equilibration possibly involving more than one of the types of reactions presented in Schemes I and II. It is clear that ion **12** must interconvert to a large degree *via* a methylcyclobutenium intermediate which is of sufficient lifetime and planarity to permit conformational equilibration, thereby time averaging the geminal methylene protons. Ion **1** is much like **12** with the cyclobutyl ion **3** being relatively less stable and apparently of insufficient lifetime and/or too nonplanar to invert. In a preliminary communication[2] we considered that the cmr data presented in this study of ion **1** could be equally accommodated by equilibrating bisected ions **7**. Further considerations given in the preceding discussion have now led us to exclude this possibility.

The geometry of the cyclobutyl ion in Scheme II can be considered as that of ion **17**-X. Stability may be enhanced by interaction of the backside of the C_3–H_3 sp^3 orbital with the empty carbenium carbon p orbital at C_1.[4c,10b,40] An analogous situation has been observed for stabilization of the trivalent 2-substituted 2-norbornyl cations.[32]



17-X

Both the nonequivalence of the methylene protons in **1** and the equivalence of the methylene protons in **12** can be explained by the same equilibrium scheme. For **17**-H (**1**) the C_1–C_3 interaction in the cyclobutenium intermediate (or transition state) **3** is strong and does not permit interconversion of the methylene protons. However, for **17**-CH_3 (*i.e.*, as in **12**) the tertiary stabilization of charge at C_1 enables the ion to be less puckered, the C_1 carbon demanding less stabilization. The C_1–C_3 interaction is therefore weak and there is sufficient lifetime for this intermediate cyclobutyl ion to undergo the conformational equilibration necessary for the observed time averaging of the methylene protons, which may be as well a more facile process due to the anticipated greater planarity of this ion.

It was suggested by one of the referees that a mixture of ions of the types **2** and **3** in both cases **1** and **12** could explain the cmr data obtained. In the case of ions **1**, competing primary (**2**) and secondary (**3**) ions have given methine cmr shifts estimated as δ +118 and −125 ppm, respectively. The obtained value of δ +85 would imply a mixture of 13–14% ion **3**. For ions **12** the estimates of 1-methyl analogs of **2** (δ +108) and **3** (δ −142) have been made and comparison with the observed experimental value of δ +33 would imply a mixture of 30% of the tertiary methylcyclobutyl ion, the remainder being the primary ion analog of **2**, probably having about the same stability as unsubstituted **2** ions. The implication of these calculations is that the tertiary methylcyclobutyl ion is barely different in stability from the secondary cyclobutyl ion. We feel this to be unlikely.[41] The small differences based on the foregoing assumptions in stabilities of the tertiary and secondary cyclobutyl ions should enable the ring conformational equilibration to be observed in **1** as well as in **12**, thereby effecting time averaging of the geminal protons. This, too, is not observed. All of the arguments in favor of structures **5** are made from model ions of proven structures to which we are directly relating **1** and **12**.

The 1-phenylcyclobutyl cation **15** is the first reported long-lived cyclobutenium ion (cyclobutyl cation). Undoubtedly positive charge delocalization into the phenyl rings is appreciable, but the ion is a trivalent (classical) carbenium ion.

In summary, we set out to prepare long-lived cyclopropylcarbinyl and cyclobutyl cations with the hope of establishing their structures by nmr spectroscopy. We expected that this study would add further to the direct experimental evidence for the structure of carbocations including differentiation of trivalent carbenium ions from penta- and/or tetracoordinated carbonium ions. Both of these objectives have been met. We have obtained well-defined spectral data of long-lived ions and have been able to interpret the results in a manner which provides further support for distinction between the two distinct classes of carbocations.[1b]

As is the case for the 2-norbornyl system,[32] both classes of ions, the unsubstituted norbornyl and cyclobutyl ions and the three-center bound carbonium ions, are observed in the cyclobutyl system. Phenyl substitution in both cases allows formation of tertiary carbenium ions. A methyl group in the 2 position of the norbornyl system gives the "classical" ion with some σ delocalization, while in the cyclobutyl system methyl substitution is not effective in lowering the energy of the carbenium ion **3**-type structure enough to make it the most stable species. Methyl substitution does, however, lower the energy of this species appreciably relative to the unsubstituted ion **1**, causing its intermediacy in the rearrangement of the $C_{2,3}$-cyclopropylcarbonium ions to have sufficient lifetime for ring conformational equilibration to occur.

Experimental Section

Cyclobutanol was obtained from Sapon Laboratories.

Cyclopropylcarbinol and **methylcyclopropylcarbinol** were obtained from Aldrich Chemical Co.

Dimethylcyclopropylcarbinol was a sample used in a previous study.[24b]

1-Methylcyclobutanol was prepared by reaction of methylmagnesium iodide and cyclobutanone[42] (Aldrich). The product distilled at 34–37° (7 mm) (lit.[42] bp 118.3 (765 mm)).

Methyl-1-methylcyclopropylcarbinol was prepared by lithium aluminum hydride reduction of methyl 1-methylcyclopropyl ketone[43] (Eastman). Distillation gave the product alcohol; bp 132° (lit.[43] bp 133°).

Dimethyl-1-methylcyclopropylcarbinol was prepared by reaction of 3 *N* methylmagnesium bromide in ether (Arapahoe Chemicals Inc.) and methyl 1-methylcyclopropyl ketone[44] (Eastman). Distillation gave a clear liquid, bp 134–136° (lit.[44] bp 132–133°).

1-Phenylcyclobutanol was prepared by reaction of phenylmagnesium bromide with cyclobutanone.

Crystallization from pentane of the yellow liquid product first obtained gave a slightly off-white solid, mp 38.5–41.5° (lit.[45] mp 41–42°).

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Preparation of Solutions of Cations. Most of the ions discussed were prepared from carbinol precursors. Best results were obtained by freezing approximately 60 mg of the alcohol into the wall of a test tube containing about 1.5 ml of the acid solution at −78°. The alcohol is then gently washed into solution. Careful agitation at the start is usually required. Complete mixing is accomplished with a vortex mixer. Typical acid solutions were ~1:3 (v/v) SbF_5–SO_2ClF and saturated solutions (prepared at −10°) of SbF_5 in SO_2.

Quenching of Solutions of Ions. About 0.3 g of precursor alcohol was ionized as usual at −78°. The solution was allowed to stand at this temperature for 3.0 hr, at which time pmr showed no precursor remaining. The solution was added dropwise to a rapidly stirred solution of 100 ml of ice–water containing 5.0 g of K_2CO_3 and 25 ml of diethyl ether. The aqueous layer was repeatedly extracted with ether and reduced in volume. Glpc was generally carried out on a Perkin-Elmer Model 226 gas chromatograph using a 50 × 0.01 in. capillary polypropylene glycol "R" column at 60°. Products were identified by comparison with authentic samples. Ratios of cyclobutanol to cyclopropylcarbinol varied (see text).

Nuclear Magnetic Resonance Spectra. Proton spectra were recorded at 60 and 100 MHz on Varian Associates Model A56-60A and HA-100 spectrometers. Capillary TMS was used as reference. ^{13}C spectra were obtained by the indor method. The general technique employed has been described previously.[46] We have since modified the instrumentation. The proton (monitoring) signal was obtained at 100 MHz with a Varian HA-100 spectrometer. The 25.1-MHz frequency was obtained from a Monsanto 3100 Digital Frequency Synthesizer. Frequency sweeping was accomplished by means of the voltage ramp of a C-1024 time-averaging computer which in some cases was also used for signal accumulation by rapid (30–60 Hz sec^{-1}), repetitive sweeping through the 25.1 MHz region. ^{13}C shifts were calculated with respect to $^{13}CS_2$. Negative shifts indicate resonances downfield from $^{13}CS_2$.

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Friedel–Crafts Chemistry. VII.[1] The Methyl and Ethyl Fluoride–Antimony Pentafluoride Complexes. Structure and Alkylating Ability. Evidence for the Intermediacy of the Ethyl Cation

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Abstract: The $CH_3F{\rightarrow}SbF_5$ and $CH_3CH_2F{\rightarrow}SbF_5$ complexes were prepared at low temperature in SO_2 solution. Their structure was studied by spectroscopy (^1H, ^{13}C, ^{19}F nmr, laser Raman). Spectroscopic and isotopic labeling experiments show the intermediacy of the ethyl cation in solutions of ethyl fluoride and antimony pentafluoride. The alkylating power of methyl and ethyl fluoroantimonates is unmatched by that observed for any previously reported methylating or ethylating agent.

The interaction of primary and secondary alkyl halides with Lewis acid halides has been a topic of extensive study.[2–4] Literature of Friedel–Crafts alkylation reactions has indicated that in the presence of acid catalysts, alkyl halides undergo either limiting formation of an alkyl halide–Lewis acid halide complex or carbenium ion formation through heterolytic cleavage of the carbon–halogen bond. For these two possibilities, Friedel–Crafts alkylation can occur either *via* a displacement reaction of the alkyl halide–Lewis acid halides complex or a direct alkylation by the carbenium ion, respectively. In recent years, we found that tertiary and secondary alkyl halides in antimony pentafluoride solution generally form stable carbenium ion fluoroantimonates. We have also shown[3r] that an excess of primary (and, under certain conditions, secondary or even tertiary) alkyl halides (other than fluorides) yields dialkylhalonium ion salts with antimony pentafluoride. No primary alkylcarbenium ions were, however, ever observed.

Infrared spectroscopic studies of methyl chloride in $SnCl_4$ and $SbCl_5$ solution[3h] and studies of methyl fluoride in BF_3 solution[3d,n] indicate that these exist as slightly polarized donor–acceptor complexes. From their kinetic study, Brown, Pearsall, and Eddy[3b] concluded that Lewis acid halide catalyzed alkylation of

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