pK_1 of phthalic acid. Next, the COOH group in the 3 position ionizes, pK_2 approximating that of benzoic acid. Finally, the 2-COOH group ionizes, pK_3 being close to that of pK_2 of phthalic acid.[20] Martin[21] titrated a number of aliphatic and aromatic tri- and tetracarboxylic acids in DMSO with an aqueous solution of tetrabutylammonium hydroxide and has reported half neutralization potentials. Applying our pK scale (in anhydrous DMSO) to his data, Martin found for 1,2,3-benzenetricarboxylic acid $pK_1 = 7.0$ (which appears to be 1 or 2 units too large), $pK_2 = 11.2$ (pK of benzoic acid is 11.1), and $pK_3 = 16.2$ and for 1,2,4-benzenetricarboxylic acid 5.2, 11.4, and 15.8, respectively.

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References and Notes

(1) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **97**, 1376 (1975).
(2) M. K. Chantooni, Jr., and I. M. Kolthoff, *J. Phys. Chem.*, **79**, 1176 (1975).
(3) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **98**, 5063 (1976).
(4) F. Westheimer and O. Benfy, *J. Am. Chem. Soc.*, **78**, 5309 (1956).
(5) A. Behr and W. A. van Dorp, *Justus Liebigs Ann. Chem.*, **172**, 263 (1874).
(6) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **87**, 4428 (1965).
(7) I. M. Kolthoff, M. K. Chantooni, Jr., and Ş. Bhowmik, *J. Am. Chem. Soc.*, **90**, 23 (1968).
(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Wiley, New York, N.Y., 1959, p 128.
(9) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **93**, 3843 (1971).
(10) M. K. Chantooni, Jr., and I. M. Kolthoff, *J. Phys. Chem.*, 77, 527 (1973); **78**, 839 (1974).
(11) D. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).
(12) L. McCoy, *J. Am. Chem. Soc.*, **89**, 1673 (1967).
(13) L. Eberson, "Chemistry of Carboxylic Acids and Esters", S. Patai, Ed., Interscience, New York, N.Y., 1969, p 280.
(14) S. Forsen, *J. Chem. Phys.*, **30**, 852 (1959).
(15) Spectra available from the authors upon request.
(16) W. T. Davison, *Chem. Ind.* (*N.Y.*), 408 (1953).
(17) Y. Okaya, *Acta Crystallogr.*, **19**, 879 (1965).
(18) H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy", Wiley, New York, N.Y., 1962, p 404.
(19) I. M. Kolthoff and M. K. Chantooni, Jr., *Anal. Chem.*, **39**, 1080 (1967).
(20) A description of more exact calculations is available from the authors upon request.
(21) J. Martin and J. Duperis, *Bull. Soc. Chim. Fr.*, 1033 (1969).

1-Methylcyclopropylcarbinyl Cations[1]

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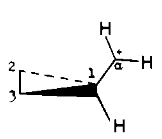
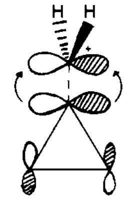
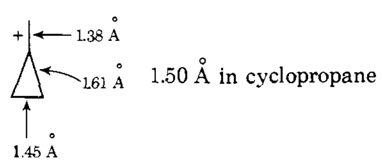
Abstract: A series of 1-methylcyclopropylcarbinyl cations have been prepared and their proton and ^{13}C NMR spectra investigated under stable ion conditions. The parent ion was found to be best represented in terms of a dynamic equilibrium involving significant contributions from both the 1-methylcyclobutyl cation and the set of three equivalent δ-delocalized 1-methylcyclopropylcarbinyl cations. Such a conclusion is supported by ab initio molecular orbital calculations at the split-valence-shell 4-31G level. Tertiary ions studied are static carbenium species and adopt the bisected geometry characteristic of cyclopropylcarbinyl cations. Destabilization of the bisected geometry due to eclipse of the C_1 methyl and one of the groups attached to C_α is undetectably small and, in fact, the 1-methylcyclopropyl group is slightly more effective than a cyclopropyl group with respect to charge delocalization.

Numerous studies of the solvolysis of cyclopropylcarbinyl derivatives[7,8] and direct observation of cyclopropylcarbinyl cations under stable ion conditions[9-11] have demonstrated the remarkable ability of a three-membered ring to stabilize an electron-deficient center to which it is attached. Indeed, in the gas phase, the cyclopropyl group has been shown to be even slightly more effective than a phenyl ring in stabilizing a tertiary (dimethyl substituted) carbocation center.[12] This stabilization arises primarily from the ability of the C_1–C_2 and C_1–C_3 linkages of the cyclopropyl group to donate electron density onto an atom to which it is attached. In the language of molecular orbital theory, what we are seeing is the interaction between the antisymmetric member of the degenerate set of "Walsh" orbitals on cyclopropane[13] and an empty p function at the formal center of positive charge. The transfer of electrons which results—from cyclopropane to C^+—results not only in a considerable shrinkage of the connecting linkage (i.e., the formation of a partial double bond), but also to sizable distortions within the small ring itself.[14] In particular, two of cyclopropane's carbon-carbon linkages have elongated, while the third has shortened. The previously reported theoretical geometrical structure for the parent cyclopropylcarbinyl cation

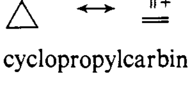




fully substantiates these contentions.[15] In simple valence bond terms, what such geometry suggests is the significant contri-

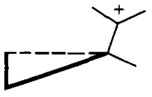


bution of resonance structures of the form (i.e. vinylated ethylene) shown in (1). It should be emphasized that although the


(1)

picture of the primary cyclopropylcarbinyl cation which arises from out of the molecular orbital calculations is only topologically a "classical" one (that is, of substitution at C^+ by a cyclopropyl group), in fact the system is one in which a high degree of σ-electron delocalization has occurred. Whether we choose to regard this σ delocalization (from the σ bonds of the small ring into a vacant p orbital at C^+) as sufficient (or insufficient) to render the ion "nonclassical" is strictly a matter of personal preference. It only points to the inadequacy of the "classical-nonclassical" differentiation of carbocations. Further care should be exercised to what meaning is given, in any, besides the topological attachment of the carbocation center to a single carbon atom, to the term "primary" ion. Clearly the degree of charge delocalization is vastly different in the benzyl, cyclopropylcarbinyl, and methyl cations.

The available experimental evidence[10] on secondary and tertiary cyclopropylcarbinyl cations indicates a sizable preference for the cyclopropane ring to adopt a conformation in which it bisects, rather than eclipses, the vacant p orbital at the forma center of positive charge. This preference is also easily rationalized within the framework of the molecular orbital theory.[14] Thus, whereas overlap, and hence interaction, between the antisymmetric Walsh component and the vacant orbital at the carbocation center is significant and leads to a high degree of energetic stabilization, that involving the complementary "symmetric" function is far smaller. This is simply because this component of the degenerate set is primarily localized on those atomic centers which are furthest removed from the point of attachment of the small ring to the carbocation center. The energy difference between bisected and eclipsed structures (i.e., the barrier hindering rotation about the ring-carbocation center linkage) has been estimated experimentally for one system, the tertiary dimethylcyclopropylcarbinyl cation, by investigation of the temperature dependence of its proton NMR spectrum.[16] The value which results, 13.7 kcal/mol, is quite close to the 12.3 kcal/mol energy obtained by molecular orbital calculations at the minimal basis set STO-3G level.[17] This same theoretical method yields a larger, 25.7 kcal/mol, barrier hindering rotation in the parent system.[17] All other semiempirical and ab initio molecular orbital procedures which have been applied to the same problem have yielded similar results.[18-20]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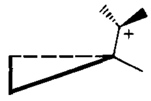
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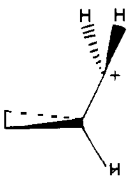
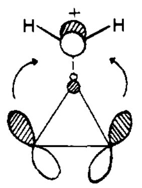
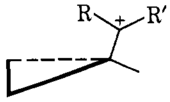




Although the molecular orbital calculations completed to date seem to indicate that the primary or parent cyclopropylcarbinyl cation, **1** (R = R′ = H) exists in the form of the bisected structure described above, it should be noted that the ^1H and ^{13}C NMR spectra of the species under stable ion conditions in superacid media are not readily interpretable as such.[10,21] Rather, these data have been interpreted as arising from a degenerate equilibrium of rapidly equilibrating σ-delocalized ions of different geometrical structure. That is to say, the experimental data may not, in any obvious manner, be easily molded into the theory's picture for the system,[17] that is, three equivalent bisected cyclopropylcarbinyl cations separated from each other by only small interconversion barriers (2).



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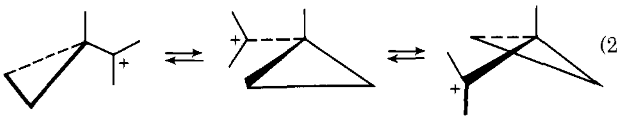
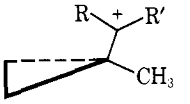


(2)

In order to attempt reconciliation of the differences between the experimental and theoretical data on the cyclopropylcarbinyl cations, we have carried out a joint study on the related 1-methylcyclopropylcarbinyl cations **2** (R = R′ = H, R = H, R′ = CH_3, R = R′ = CH_3). Our results are presented in this paper.



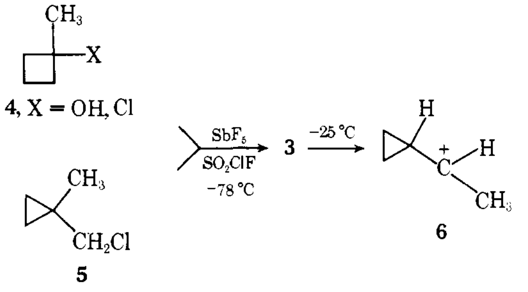
2

Parent ion **2** is of considerable interest for a number of reasons. For one, we might expect that its dynamic behavior would be very similar indeed to that of the parent unsubstituted cyclopropylcarbinyl system. Thus, its study might provide us with an opportunity to reconcile the differing observations of the experiment and theory with regard to the properties of the parent ion. The differences between the two ions, which develop because of the methyl substituent, are also worthy of further scrutiny. While we might expect that the methyl group would have little overall energetic effect on the bisected cyclopropylcarbinyl cation other than to destabilize this conformer slightly relative to the eclipsed, it should provide a healthy stabilization to another structural isomer on the potential surface, the methylcyclobutyl cation. Recall that the NMR spectra of the parent cyclopropylcarbinyl cation[10] showed no contribution from a stable cyclobutyl cation. Such a species was implicated by the quantitative molecular orbital calculations,[17] however, to be one possible low energy transition state for the degenerate interconversion of cyclopropylcarbinyl forms. The cyclobutyl cation is, of course, also quenched out in solvolytic studies.[7]

We have also chosen to study a number of simple derivatives of the 1-methylcyclopropylcarbinyl cation, specifically situations in which additional stabilization is provided by methyl, hydroxy, and phenyl substituents at the formal carbocation center. The results, when compared to those for the analogous cyclopropylcarbinyl cations, should provide evidence for or against the participation of a methyl group at C_1 in the chemical reactivity and charge distributions of these ions.

Results and Discussion

The parent 1-methylcyclopropylcarbinyl cation (**3**) can be generated either from 1-methylcyclobutanol (**4**-OH), as employed in this study,[10] 1-chloro-1-methylcyclobutane (**4**-Cl),[22] or 1-chloromethyl-1-methylcyclopropane (**5**)[22] with SbF_5 in SO_2ClF at −78 °C (eq 3). The ion is stable at temperatures up to −25 °C, where a slow isomerization ($E_a \simeq 20$ kcal/mol)



(3)

Table I. ^1H NMR Data[a] for 1-Methylcyclopropylcarbinyl Cations, Their Corresponding Cyclopropylcarbinyl Cations, and Ions Formed by Ring Opening of These Ions

Ion	H_1	H_2, H_3	C_1-CH_3	Additional
3[b]		3.89	2.87	$J_{CH_2\text{-}CH_3} = 0.9$
8[c]	6.50	exo, 4.64; endo, 4.21		H_α; exo, 4.64; endo, 4.21
				J_{H_1}, exo = 8.0, J_{H_1}, endo = 6.5
10[d]		3.80 (mult)	1.86	C_α-CH_3; 2.77, 3.11
11[c]	3.83	exo, 3.68; endo, 3.57		C_α-CH_3; 2.70, 3.18
18a[e]		2.22, 2.45	1.50	C_α-CH_3; 2.45
18b[e]		2.22, 2.45	1.50	C_α-CH_3; 2.99
18[f]		2.17, 2.36	1.43	C_α-CH_3; 2.55

[a] Chemical shifts are in parts per million from external (capillary) Me_4Si, coupling constants are in hertz. [b] Data from ref 22. [c] Data from ref 10. [d] In SbF_5-SO_2ClF at −75 °C. [e,f] In FSO_3H-SO_2ClF at −95 and −15 °C respectively.

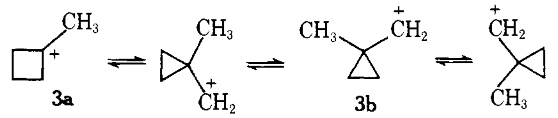
Table II. ^{13}C NMR Data[a] for 1-Methylcyclopropylcarbinyl Cations, Their Corresponding Cyclopropylcarbinyl Cations, and Ions Formed by Ring Opening of These Ions

Ion	C_1	C_α	C_2, C_3	C_1-CH_3	Additional
3[b]	163.25		48.55	25.35	
			(176.7)	(129.5)	
8[c]	108.2		57.6		
	(180)		(180)		
10[b]	64.7	276.6	61.7	20.4	C_α-CH_3; 36.2 (≃130),[d] 31.4 (≃130)[d]
			(174.9)	(130.8)	
11[c]	56.4	281.7	53.4		C_α-CH_3; 38.7 (132), 28.8 (132)
	(187)		(176)		
18a[e]	36.2	236.15	32.5	16.0	C_α-CH_3; 21.65
18b[e]	33.5	241.85	38.9	17.4	C_α-CH_3; 28.65
18[f]	35.65	238.4	35.6	17.15	C_α-CH_3; 24.34 (132.5)
			(131.0)	(131.0)	
20a[e]	29.75	240.7	30.75		C_α-CH_3; 27.6
20b[e]	20.2	237.75	25.2		C_α-CH_3; 27.6

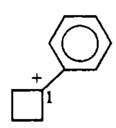
[a] Chemical shifts are given in parts per million from external (capillary) Me_4Si; coupling constants (in parentheses) are in hertz. [b] In SbF_5-SO_2ClF at −75 °C. [c] Data from ref 25. [d] Overlapping quartets. [e,f] In SbF_5-SO_2ClF at −95 and −15 °C, respectively.

occurs to form the α-methylcyclopropylcarbinyl cation (**6**).[22]

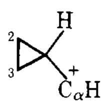
That **3** is not a static ion can clearly be seen from its NMR spectra. The ^1H NMR spectrum (Table I) consists only of two resonances, δ 2.87 and 3.89, ratio 3:6, mutually coupled by 0.9 Hz. The trideuteriomethyl derivative, generated from **4**-Cl, C_1-CD_3, exhibits only a single resonance at δ 3.89 and no proton-deuterium scrambling is observed even after extended periods.[22] Saunders and Rosenfeld concluded from the above ^1H NMR data that **3** exists as a rapid equilibrium between the 1-methylcyclobutyl cation (**3a**) and the three degenerate 1-methylcyclopropylcarbinyl cations (**3b**)[22] (eq 4). The ^{13}C NMR parameters (Table II) are certainly consistent with this conclusion, since only three resonances, δ 163.25 (C_1), 48.55 (C_2, C_3, C_α), and 25.35 (CH_3) are observed. $^1J_{CH}$ for the CH_3 group, 129.5 Hz, is characteristic of a methyl group sharing a positive charge in equilibrating ions.[23] The resonance position of C_1 is nearly equidistant from the 1-methylcyclopentyl ion (δC^+ 335.8)[24a] and an estimated value of 10 ppm for C_1 in 1,1-dimethylcyclopropane,[24b] suggesting approximately equal contributions from **3a** and **3b**. Note, however, that derivatives of either **4** or **5** solvolyze exclusively to products derived from **3a**. The only static cyclobutyl cation for which NMR data have been reported is the 1-phenylcyclobutyl cation (**7**);[6] C_1 resonates at 273 ppm, a position very similar to other 1-phenylcycloalkyl cations.



3a **3b** (4)



7 δC_1 = 273 ppm[6]



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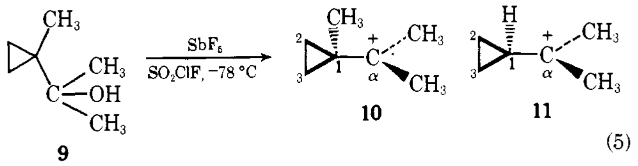
The differing nature of equilibrating ion **3** and that of the previously extensively studied parent cyclopropylcarbinyl cation **8**[10] can clearly be seen from C_2, C_3 and C_α in **3** lose their relative identity (single chemical shift), while **8** exhibits separate exo and endo resonances (Table I). This fact alone rules out any contribution from a planar cyclobutyl cation intermediate to **8**, since this would presumably, as in **3**, result in loss of identity of the exo and endo proton resonances. The ^{13}C NMR data are, however, surprisingly consistent, since it would be expected that replacement of H_1 in **8** by CH_3 (to give **3**) would result in shielding of the C_2, C_3, and C_α carbon resonance and deshielding of C_1 due to increased charge development at C_1, exactly as observed (Table II). The $^1J_{CH}$ value for $C_2 = C_3$, C_α in **3**, 176.7 Hz, is comparable to that in **8** (180)[21] and static classical cyclopropylcarbinyl cations (e.g., **10**, **11**, Table II),[25] further emphasizing the difficulty of using this parameter to distinguish the structures of cations derived from cyclopropylcarbinyl precursors.[26]

The results of the ab initio molecular orbital calculations are in qualitative agreement with the experimental data in suggesting that both the 1-methylcyclopropylcarbinyl and methylcyclobutyl cations are stable forms on the $C_5H_9{}^+$ potential surface. At the split-valence-shell 4-31G level of theory,[27] the latter is some 6.5 kcal/mol the lower in energy, although this difference (which is larger than expected from the experimental NMR data) is likely to be reduced somewhat by extension of the basis set representation to allow for polarization-type functions at the carbon centers. For example, introduction of polarization functions reduces the energy difference between cyclobutane and methylcyclopropane from 1.9 kcal/mol at the 4-31G level to 0.7 kcal/mol.[29] A somewhat larger reduction (from 23.4 to 19.0 kcal/mol) has been noted for the cyclobutene-1-methylcyclopropene pair.[29] Although the potential barrier separating the two $C_5H_9^+$ isomers has not as yet been determined precisely, the calculations along the interconversion pathway which have been performed indicate that it is rather small (~2-5 kcal/mol).

We find that the equilibrium structure for the methylcyclobutyl cation[30] incorporates a planar as opposed to a puckered carbon skeleton, in contrast to the results of calculations regarding the geometry of the unsubstituted system. In the instance, puckering of the four-membered ring to an optimum dihedral angle of 122.4° was predicted to lead to an energy lowering of 2.6 kcal/mol. Contribution of planar 1-methyl-substituted ion to the equilibrating system is consistent with the proton NMR spectral data for the system, in which only two resonances appear, one corresponding to the three methyl protons, the other to the six hydrogens on the small ring.

Further evidence in support of the contention that the 1-methylcyclopropylcarbinyl cation is best described in terms of a dynamic equilibrium rather than a static ion is presented in Figure 1. Here we have plotted experimental ^{13}C chemical shifts at C^+ (relative to Me_4Si) for a number of tertiary carbocations, against STO-3G calculated[31] π charges. The ions chosen are all systems where geometrical structure has been assigned unequivocally. Even though such direct charge-shift comparisons have repeatedly drawn criticism,[32] the high degree of correlation uncovered here is not surprising. That is to say, the ions involved are all of a similar enough nature that one might hope for considerable cancellation of the factors other than charge distribution which go into the makeup of the chemical shift. The point to be made is that if the calculated π charge for the methylcyclobutyl cation—also a tertiary system—is fixed to the line, the chemical shift which results (335 ppm) is far removed from the actual experimental value. On the other hand, the experimental shift (163.3 ppm) is intermediate between the estimated value for C^+ in the methylcyclobutyl cation and that which characterizes C_1 in the static tertiary cyclopropylcarbinyl cations **1** and **2** ($R = R' = CH_3$).

The good agreement between experiment and theory regarding the structure of the 1-methyl-substituted cyclopropylcarbinyl cation also provides some insight into the nature of the parent ion. Both ions clearly are rapidly equilibrating, involving highly σ-delocalized systems. Whereas to the former the 1-methyl-1-cyclobutyl cation makes a significant contribution, to the latter the corresponding parent cyclobutyl cation, being a much more energetic species, does not. The likely importance of solvent-solute interactions to differing ions must also be considered. 2-(1-Methylcyclopropyl)propan-2-ol (**9**) ionizes smoothly in SbF_5-SO_2ClF at −78 °C to give the tertiary 1,α,α-trimethylcyclopropylcarbinyl cation (**10**) (eq 5). The ^1H (Table I) and ^{13}C (Table II) NMR data for **10** are characteristic of a tertiary classical cyclopropylcarbinyl cation and are readily rationalized by comparison with data for the α,α-dimethylcyclopropylcarbinyl cation (**11**, Tables I and II). Both **10** and **11** exhibit separate ^1H and ^{13}C NMR resonances for each of the *gem*-dimethyl groups, clearly implicating a bisected geometry (as shown above) for these ions. Solutions of **10** can be heated to −15 °C and over the temperature range −78 to −15° the ^1H NMR spectrum shows a marked temperature dependence. The resonances due to the ring and C_1-CH_3 protons sharpen as the temperature rises, presumably due to decreased viscosity broadening, while the *gem*-CH_3 proton resonances broaden and nearly coalesce at −15 °C. The latter observation arises from increased rotation, on the NMR time scale, about the C_1-C_α bond. Unfortunately, decomposition of **10** was too rapid above −15 °C to observe complete coalescence and determine the rotational barrier, but a value of 12-15 kcal/mol seems a reasonable estimate from the temperature dependence. **11** decomposed above −30 °C,[33] but the rotational barrier was determined by double resonance experiments.[16] The barrier for **11**, 13.7 ± 0.4 kcal/mol, is comparable to our estimate for **10** and suggests that the C_1-CH_3 group introduces no appreciable destabilization of the bisected geometry.



9 **10** **11** (5)

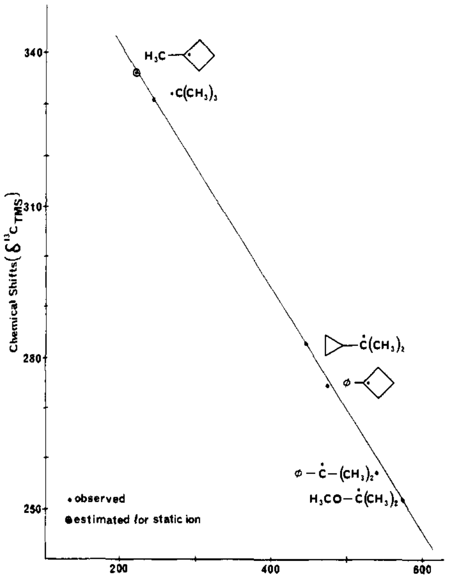
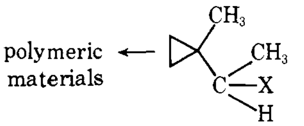


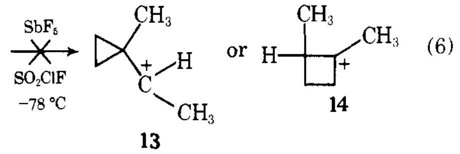
Figure 1. Plot of carbocation $^{13}C^+$ shifts against STO-3G calculated π charges.

In fact, comparison of the ^{13}C NMR data for **10** and **11** (Table II) reveals that more charge is absorbed by the cyclopropyl ring in **10**; $C_2 = C_3$ (Table II) (and also $H_2 = H_3$, Table I) are more deshielded in **10** than **11**, while the reverse is true for the carbenium carbon (C_α) resonances. Although interpretation of the ^{13}C NMR data in terms of quantitative differences in charge distribution between **10** and **11** is not possible,[34] the conclusion that the 1-methylcyclopropyl group is slightly better able to delocalize positive charge than a cyclopropyl group is consistent with solvolytic data.[8,35,36] Not unexpectedly, methyl groups at C_α in particular, and at $C_2 = C_3$, give rise to larger rate enhancements.[8]

Dissolution of 1-(1-methylcyclopropyl)ethanol (**12**-OH) or its chloride (**12**-Cl) in SbF_5-SO_2ClF at −78 °C yielded a



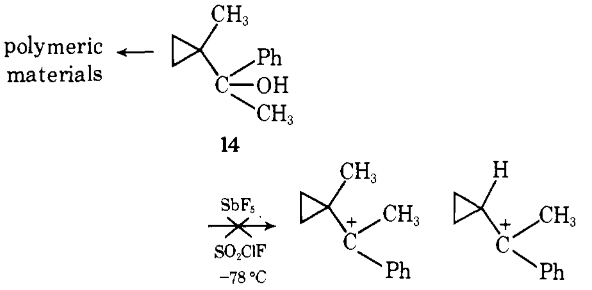
12, X = OH, Cl



13 **14** (6)

^{1}H NMR spectrum which could be attributed to neither the secondary cyclopropylcarbinyl cation (**13**), 1,2-dimethylcyclobutyl cation (**14**), nor equilibration between these species (eq 6). Instead, the broadness of the spectrum suggested that only polymeric materials were formed. Treatment of **12**-OH with "normal" protic acids yields products derived only from **14**;[37] evidently these ions are not stable in SbF_5-SO_2ClF, possibly due to ring opening reactions with subsequent polymerization.[38]

Similarly, dissolution of 1-(1-methylcyclopropyl)-1-phenylethanol (**14**) in SbF_5-SO_2ClF at −78 °C yielded a solution whose ^{1}H NMR spectrum showed the presence only of polymeric materials with no **15** being detectable (eq 7).



14

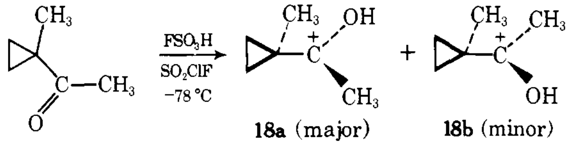
(7)

15 **16**

The inability to observe **13** and **15** is in sharp contrast to the ease of generation of their demethylated analogues **6**[10,22] and **16**[33] under these conditions. We feel that although there may be some loss of stability for **13** and **15** relative to **6** and **16**, the predominant factor in their differing behavior is the greater ease for ring opening of the 1-methylcyclopropyl group compared to the cyclopropyl group yielding allylic ions which are not stable in SbF_5-SO_2ClF.[38]

Dissolution of methyl 1-methylcyclopropyl ketone (**17**) in FSO_3H-SO_2ClF at −78 °C yielded a deep yellow solution, the ^{1}H NMR spectrum of which contained only two uncoupled methyl groups, an AA^1XX^1 pattern for the cyclopropyl ring protons and the deshielded hydroxyl resonance (Table I). This spectrum is consistent with the protonated ketone structure; lowering of the temperature below −70 °C led to broadening of all signals and at −100 °C the deshielded methyl resonance (δ 2.55) split into a major component at δ 2.45 (coincident with the deshielding cyclopropyl proton signals) and a minor component at δ 2.99. Separate resonances for major and minor components for the C_1-CH_3 or cyclopropyl resonances could not be resolved and further lowering of the temperature led only to viscosity broadened spectra.

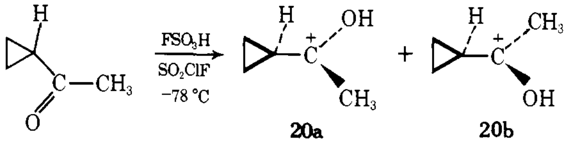
The spectral changes described above result from freezing out of the rotameric pair **18a** and **18b** (eq 8). Since the proton resonance of the C_α-CH_3 in the major isomer was shielded by 0.54 ppm relative to the minor isomer, the major isomer was assigned as **18a**, where the C_α-CH_2 lies in the shielding zone of the cyclopropyl ring.[39] The ^{13}C NMR spectrum at −95 °C also shows the presence of two isomers in the ratio 3.5:1 (Table II). At −70 °C, the spectrum was extensively broadened due to the coalescence of the respective carbon pairs, while the sharp spectrum at −15 °C (Table II) indicated that rotation about the C_1-C_α bond was fast on the NMR time scale. The ^{13}C NMR spectrum of methyl cyclopropyl ketone (**19**) in FSO_3H-SO_2ClF at −90 °C also shows the presence of the two rotamers (**20a, 20b,** Table II)[40] in the ratio 4:1 and a similar temperature dependence to that described above for **17** in FSO_3H-SO_2ClF (eq 9).



(8)

17

18a (major) **18b** (minor)



(9)

19

20a **20b**

The ^{13}C chemical shifts for **18a** compared to **20a** can be seen to follow the same trends described previously for **10** and **11.** The carbenium carbon (C_α) in **18a** is more shielded than **20a,** while the reverse is true for the cyclopropyl carbons $C_2 = C_3$. Comparison of data for the minor isomers reveals that both C_α and $C_2 = C_3$ are more deshielded in **18b** than **20b.** Although quantitative comparisons are again not possible,[34] these results suggest an enhanced delocalization from the 1-methylcyclopropyl group relative to the cyclopropyl group. Further confirmation of this conclusion can be found from half-protonation data for **17** and **19; 17** requires 67.3% H_2SO_4 for half-protonation, while **19** requires 70.4% H_2SO_4.[41]

Conclusion

Comparison of our result for 1-methylcyclopropylcarbinyl cations with data for cyclopropylcarbinyl cations reveals many similarities, but also differences. The parent cation (**3**) exists as a dynamic equilibrium with significant contribution from the 1-methylcyclobutyl cation and σ-delocalized degenerate 1-methylcyclopropylcarbinyl cations, which is in contrast to the parent cyclopropylcarbinyl cation, in which there is no contribution from the cyclobutyl cation. Although the ^{1}H NMR parameters for **3** and **8** do show the difference between the two systems, the ^{13}C chemical shifts and cyclopropyl $^1J_{CH}$ values are not as different and clearly emphasize the care which needs to be taken for the interpretation of all parameters with respect to the structure of cyclopropylcarbinyl cations. The tertiary 1-methylcyclopropylcarbinyl cations studied are static cyclopropylcarbinyl cations and adopt the characteristic bisected geometry. The necessity to eclipse the C_1-CH_3 with one of the groups at C_α imparts no detectable instability to the bisected geometry and in fact the 1-methylcyclopropyl group is marginally better able to delocalize charge than the cyclopropyl group.

The presence of the C_1-CH_3 group appears to lead to more facile ring opening than is the case with cyclopropylcarbinyl cations. The inability to detect some of the 1-methylcyclopropylcarbinyl cations in SbF_5-SO_2ClF is most probably due to their facile ring opening.

Experimental Section

Cyclobutanone, methyl 1-methylcyclopropyl ketone (**17**), and methyl cyclopropyl ketone (**19**) were commercial samples (Aldrich). SbF_5 and FSO_3H were both doubly distilled prior to use.

1-Methylcyclobutanol (4-OH). Cyclobutanone (1 g, 0.014 mol) in anhydrous ether (5 ml) was added dropwise, with stirring, to an ice-cooled solution of methyllithium in hexane (Alfa Inorganics, 0.018 mol) diluted with anhydrous ether (5 ml). The solution was stirred overnight then worked up in the usual manner to give **4**-OH as a colorless liquid, bp 117-118 °C [lit.,[35] bp 118.3 °C (765 mm)].

1-(1-Methylcyclopropyl)ethanol (12-OH). **17** (5 g) in anhydrous ether (50 ml) was added dropwise, with stirring, to a suspension of lithium aluminum hydride (2 g) in anhydrous ether (50 ml). The solution was stirred overnight, worked up by addition of water, and the ether dried over magnesium sulfate. Removal of ether followed by distillation afforded **12**-OH as a colorless liquid, bp. 133 °C (lit.[10] bp 132 °C).

2-(1-Methylcyclopropyl)propan-2-ol (9). **17** (5.0 g, 0.049 mol) in anhydrous ether (50 ml) was added dropwise with stirring to an ice-cooled solution of methyllithium in hexane (Alfa Inorganics, 0.055 mol) diluted with anhydrous ether (50 ml). After stirring overnight, workup as for **12**-OH gave **9** as a colorless liquid, bp 134–135 °C (lit.[10] bp 134–136 °C).

1-(1-Methylcyclopropyl)-1-phenylethanol (14). **17** (3.0 g, 0.03 mol) in anhydrous ether (20 ml) was added dropwise, with stirring, to an ice-cooled solution of phenyllithium in hexane (0.04 mol) diluted with anhydrous ether (30 ml). After stirring overnight at room temperature, the solution was worked up as for **12**-OH to give **14** as a colorless liquid, bp. 68–69 °C (0.4 mm).

Preparation of Ions. The precursor (200 mg) was dissolved in SO_2ClF (1.5 ml) and the solution cooled to −78 °C. Portions of this solution were added dropwise, with rapid shaking (Vortex mixer) to a solution of SbF_5 (0.75 ml) in SO_2ClF (1.25 ml) at −78 °C (acetone-dry ice slurry). After complete addition, the sample was transferred by precooled pipet to a precooled NMR tube. In cases where this did not yield the desired ion (see text), the procedure was repeated at −120 °C (ethanol-liquid nitrogen slush).

NMR Spectroscopy. ^1H NMR spectra were recorded on a Varian Associates Model A56/60A spectrometer equipped with a variable temperature probe. Chemical shifts are in parts per million from external (capillary) Me_4Si.

^{13}C NMR spectra were obtained using a Varian Associates Model XL-100 spectrometer equipped with a broad band decoupler, variable temperature probe, and interfaced with a Varian 620-L computer operating with 8192 digital points. Chemical shifts were measured from the ^{13}C signal of 5% ^{13}C enriched Me_4Si contained in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube. Coupling constants were obtained directly from the spectra recorded in the gyrogate mode. Typically, 2000–5000 transients were necessary to obtain acceptable signal to noise levels.

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References and Notes

(1) Stable Carbocations part 200. Part 199: G. A. Olah, G. K. S. Prakash, and G. Liang, *J. Org. Chem.*, **41**, 2820 (1976).

(2) Case Western Reserve University.

(3) Postdoctoral Research Associate 1973–1975.

(4) Université de Paris-Sud.

(5) University of California, Irvine.

(6) Alfred P. Sloan Fellow, 1974–1976.

(7) For major reviews, see: (a) R. Breslow in "Molecular Rearrangements", Part 1, P. de Mayo, Ed., Interscience, New York, N.Y., 1963, Chapter 4; (b) M. Hanack and H.-J. Schneider, *Angew Chem., Int. Ed. Engl.*, **6**, 666 (1967); (c) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 26.

(8) P. v. R. Schleyer and G. W. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).

(9) For a review covering literature to early 1971, see H. G. Richey, Jr., in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 25.

(10) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Am. Chem. Soc.*, **94**, 146 (1972).

(11) G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.*, **97**, 1539 (1975), and earlier literature cited therein.

(12) J. W. Wolf, P. G. Harch, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **97**, 2902 (1975).

(13) For a discussion of the valence orbitals on cyclopropane, see: R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, **93**, 5699 (1971).

(14) For a detailed discussion, see: W. J. Hehre, *Acc. Chem. Res.*, **8**, 369 (1975).

(15) W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **94**, 5917 (1972).

(16) D. S. Kabakoff and E. Namanworth, *J. Am. Chem. Soc.*, **92**, 3234 (1970).

(17) W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **96**, 302 (1974).

(18) J. E. Baldwin and W. D. Fogglesong, *J. Am. Chem. Soc.*, **90**, 4311 (1968).

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

(20) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 6380 (1970).

(21) Cyclopropylcarbinyl cations constrained with bicyclic skeletons exists as equilibrating classical ions in some cases; G. A. Olah, G. Liang, K. A. Babiak, and R. K. Murray, Jr., *J. Am. Chem. Soc.*, **96**, 6794 (1974); **98**, 576 (1976).

(22) M. Saunders and J. Rosenfeld, *J. Am. Chem. Soc.*, **92**, 2548 (1970).

(23) D. P. Kelly, G. R. Underwood, and P. F. Barron, *J. Am. Chem. Soc.*, **98**, 3106 (1976).

(24) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972. (a) Chapter 6–11; (b) Estimated from the data for cyclohexanes in Chapter 3 and the value for 15.2 ppm for C_1 in 1,1,2-trimethylcyclopropane;[21] (c) Chapter 3.

(25) D. P. Kelly and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 3897 (1975).

(26) We believe that the conclusion stated in ref 25 should be *not* that the $^1J_{CH}$ value for $C_\alpha = C_2 = C_3$ or C_1 is more consistent with one structure *but* that this parameter cannot be used to distinguish between σ-bridged, equilibrating classical, or classical cyclopropylcarbinyl cations.

(27) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1972). All calculations have been carried out using the GAUSSIAN 70 series of computer programs.[28]

(28) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., Program No. 236.

(29) (a) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975); (b) J. S. Binkley, J. A. Pople, and W. J. Hehre, *Chem. Phys. Lett.*, **36**, 1 (1975).

(30) Structure is based on the STO-3G optimized geometry for the parent cyclobutyl cation[17] substituted by a "standard" methyl group (tetrahedral, r_{CH} = 1.09 Å). Only the dihedral angle (180°), the ring–methyl bond length (1.504 Å), and the angle which the ring–methyl bond makes with the plane of the four-membered ring (180°) have been optimized. Correspondinglythe theoretical geometry for the 1-methylcyclopropylcarbinyl cation is derived from that of the parent ion[15] by attachment of a "standard" methyl group (at the same bond angles as the hydrogen it replaced) at an optimized bond length of 1.540 Å.

(31) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(32) See, however: (a) W. J. Hehre, R. W. Taft, and R. D. Topsom, *Prog. Phys. Org. Chem.*, in press; (b) D. G. Farnum, *Adv. Phys. Org. Chem.*, **11**, 123 (1975).

(33) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5123 (1965).

(34) Replacement of H_1 (in **11**) by CH_3 (to give **10**) should give rise to deshielding of the directly attached carbon C_1 (α-substituent effect)[24c] and the three adjacent carbons ($C_2 = C_3$ and C_α (β-substituent effect).[24c] The argument for changes in the $C_2 = C_3$ and C_α resonance positions. No quantitative comparisons are possible, since precise values for these substituent effects are not available.

(35) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961); W. B. Kover and J. D. Roberts, *ibid.*, **91**, 3687 (1969).

(36) D. D. Roberts, *J. Org. Chem.*, **31**, 2000 (1966) and previous papers.

(37) M. Julia, R. Guegon, Y. Noel, and T. Song-Yu, *C. R. Acad. Sci.*, **260**, 4222 (1965).

(38) Although ring opening of cyclopropylcarbinyl cations to allyl cations occurs readily in FSO_3H-SO_2ClF to give stable ions (see section 2), in SbF_5-SO_2ClF the allyl cations thus formed are not stable and rapidly polymerize; C. D. Poulter and S. Winstein, *J. Am. Chem. Soc.*, **91**, 3649 (1969).

(39) For a discussion of shielding by cyclopropane rings, see: L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, London, 1969, pp 98–101.

(40) The spectrum of **20** in $FSO_3H-SbF_5-SO_2ClF$ had previously been reported, but no assignments were made: G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 3548 (1974).

(41) A. S. Kushner, Ph.D. Dissertation, The Pennsylvania State University, University Park, Pa., 1966, cited in ref 5.